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Environmental Pollution
Prevention Project

POLLUTION PREVENTION FOR CHEMICAL AND PETROLEUM PROCESSING INDUSTRIES

Training Manual

Prepared by

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HBI Reference No TR-96-106

Environmental Pollution Prevention
Project Number 936-5559
Contract Number PCE-5559-C-00-3021-00

May 1996

Sponsored by the U S Agency for International Development (USAID)

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CHAPTER 1
INTRODUCTION

1 1 Purpose of Manual

This manual provides an introduction to the application of pollution prevention techniques in the chemical and petroleum processing industries Chemical and petroleum processing case studies are provided in the appendices

This is the sixth manual in a series on the topic of pollution prevention The first manual, "Pollution Prevention Concepts/Applications," discusses the theory and practice of pollution prevention techniques in general terms The reader should refer to this manual for general pollution prevention methodologies and definitions The second manual, "Pollution Prevention in Metal Finishing Industries," provides a survey of the application of pollution prevention techniques within the range of metal finishing processes The third manual, "Pollution Prevention in the Textile Industry," provides an introduction to the application of pollution prevention techniques in various textile preparation and finishing processes The fourth and fifth manuals, "Pollution Prevention for Dairy Industries," and "Pollution Prevention for Fish and Shellfish Processing Industries," outline pollution prevention strategies that are applicable to the food processing industries In addition, there are plans to prepare pollution prevention manuals for the pulp and paper, tanning, mining, and printing industries

The user of this chemical and petroleum processing manual should view it as a first source in pursuing process and equipment changes in the industry The manual is intended to assist professionals in determining 1) where there might be potential for improving process efficiency and profitability in chemical and petroleum processing facilities, and 2) which alternatives are worthy of consideration for implementation Users of this manual should not rely on its contents alone to carry out specific measures, but rather seek assistance from experienced professionals in the field However, as a general rule of thumb, those process improvement measures which can be implemented at no cost or low cost, or with minimal effort should be considered first, while the more capital and labor intensive options will require more extensive review

1 2 Background

Chemical processing and petroleum refining industries generate significant amounts of pollution The chemical industry in the U S alone generated and managed over 3 trillion kilograms (kg) of production-related chemical waste in 1993

The best way to reduce pollution is to prevent it in the first place Some companies in these industries have creatively implemented pollution prevention techniques that have improved efficiency and increased profits while at the same time minimizing environmental impacts

This can be done in many ways such as reducing material inputs, re-engineering processes to reuse by-products, improving management practices, and substituting benign chemicals for toxic ones

It is critical to emphasize that pollution prevention in the chemical and petroleum industries is process specific and oftentimes constrained by site-specific considerations As such, it is difficult to generalize about the relative merits of different pollution prevention strategies The age, size, and purpose of the plant will influence the choice of the most effective pollution prevention strategy Commodity chemical manufacturers redesign their processes infrequently so that redesign of the reaction process or equipment is unlikely in the short term Here operational changes are the most feasible response Specialty chemical manufacturers are making a greater variety of chemicals and have more process and design flexibility Incorporating changes at the earlier research and development phases may be possible for them

1 3 Waste Characteristics

The major pollutants and wastes associated with organic chemical processing are ammonia, nitric acid, methanol, ethylene glycol, and acetone Those associated with inorganic processing are ammonia, hydrochloric acid, carbonyl sulfide, and manganese Petroleum wastes include ammonia, toluene, xylene, methyl ethyl ketone, propylene, and benzene

Many of these pollutants are exceedingly toxic to the environment In addition, several commonly used and manufactured chemicals are known contributors to cancerous conditions

CHAPTER 2
ORGANIC CHEMICAL PROCESSING[1]

2 1 Introduction

The industrial organic chemical sector produces organic chemicals (those containing carbon) used as either chemical intermediates or end-products For the purposes of this manual, the category of organic chemicals includes gum and wood chemicals, cyclic organic crudes and intermediates, organic dyes and pigments, and some forms of industrial organic chemicals Plastics, drugs, soaps and detergents, agricultural chemicals or paints, and allied products which are typical end-products manufactured from industrial organic chemicals, are not addressed by this discussion

The industrial organic chemical market has two broadly defined categories, commodity and specialty Commodity chemical manufacturers compete on price and produce large volumes of small sets of chemicals using dedicated equipment with continuous and efficient processing Specialty chemical manufacturers cater to custom markets, manufacture a diverse set of chemicals, use two or three different reaction steps to produce a product, tend to use batch processes, compete on technological expertise and have a greater value added to their products Commodity chemical manufacturers have lower labor requirements per volume and require less professional labor per volume

2 2 Product Characterization

The industrial organic chemical industry uses feedstocks derived from petroleum and natural gas and from recovered coal tar condensates generated by coke production The chemical industry produces raw materials and intermediates, as well as a wide variety of finished products for industry, business and individual consumers

Important gum and wood chemical products include

- Hardwood and softwood distillation products,
- Wood and gum naval stores,
- Charcoal, and

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[1] The information in this chapter is derived from the U S Environmental Protection Agency's Office of Compliance Sector Notebook Project, *Profile of the Organic Chemical Industry*, September 1995 (document # EPA/310-R-95-012) Readers should refer to that document for a comprehensive set of references and sources Contact your local EP3 Clearinghouse for a copy of the EPA document or for information on how to access it electronically via the Internet

- Natural dyestuffs and tanning materials

Important cyclic organic chemical products include

- Derivatives of benzene, toluene, naphthalene, anthracene, pyridene, carbazole, and other cyclic chemical products,
- Synthetic organic dyes,
- Synthetic organic pigments,
- Cyclic (coal tar) crudes, such as light oils and light oil products,
- Coal tar acids, and
- Products of medium and heavy oil such as creosote oil, naphthalene, anthracene and their high homologues

Important industrial organic chemical products include

- Non-cyclic organic chemicals such as acetic, chloroacetic, adipic, formic, oxalic acids and their metallic salts, chloral, formaldehyde, and methylamine,
- Solvents such as amyl, butyl and ethyl alcohols, methanol, amyl, butyl, and ethyl acetates, ethyl ether, ethylene glycol ether and diethylene glycol ether, acetone, carbon disulfide, and chlorinated solvents such as carbon tetrachloride, tetrachloroethene, and trichloroethene,
- Polyhydric alcohols such as ethylene glycol, sorbitol, pentaerythritol, and synthetic glycerin,
- Synthetic perfumes and flavoring materials such as coumarin, methyl salicylate, saccharin, citral, citronellal, synthetic geraniol, ionone, terpineol, and synthetic vanillin,
- Rubber processing chemicals such as accelerators and antioxidants, both cyclic and acyclic,
- Plasticizers, both cyclic and acyclic, such as esters of phosphoric acid, phthalic anhydride, adipic acid, lauric acid, oleic acid, sebacic acid, and stearic acid,
- Synthetic tanning agents such as sulfonic acid condensates, and
- Esters and amines of polyhydric alcohols and fatty and other acids

2 3 Industrial Process Description

This section describes the major industrial processes within the organic chemical industry, including the materials and equipment used, and the processes employed This discussion also provides a concise description of where wastes may be produced in the process and describes the potential fate (via air, water, and soil pathways) of these waste products

2 3 1 Industrial Processes in the Organic Chemical Industry

The industrial organic chemical sector includes thousands of chemicals and hundreds of

processes In general, a set of building blocks (feedstocks) is combined in a series of reaction steps to produce both intermediates and end-products Exhibit 2-1 shows the primary organic chemical building blocks (generated principally from petroleum refining), a key subset of the large volume secondary building blocks and a set of large volume tertiary building blocks Exhibit 2-2 shows the reaction types used to manufacture a sample of organic chemicals, and illustrates the large variety of processes used by the industry

Exhibit 2-1 High Volume Organic Chemical Building Blocks

Primary Building Block	Secondary Building Block	Tertiary Building Block
Ethylene	Ethylene dichloride Ethylene oxide Ethylbenzene	Vinyl chloride Ethylene glycol Vinyl acetate
Propylene	Propylene oxide Acrylonitrile Isopropyl alcohol	 Acetone
Benzene	Ethylbenzene Cumene Cyclohexane	Styrene Phenol Acetone Adipic acid
Methanol	Acetic acid Formaldehyde Methyl t-butyl ether	Vinyl acetate
Toluene		
Xylenes p isomer	 Terephthalic acid	
Butadiene		
Butylene		

The typical chemical synthesis process involves combining multiple feedstocks in a series of unit operations The first unit operation is a chemical reaction Commodity chemicals tend to be synthesized in a continuous reactor while specialty chemicals usually are produced in batches Most reactions take place at high temperatures, involve metal catalysts, and include one or two additional reaction components The yield of the reaction will partially determine the kind and quantity of by-products and releases Many specialty chemicals require a series of two or three reaction steps Once the reaction is complete, the desired product must be separated from the by-products by a second unit operation A number of separation techniques such as settling, distillation or refrigeration may be used The final product may be further processed, by spray drying or pelletizing for example, to produce the saleable item Frequently, by-products are also sold and their value may alter the process economics

Exhibit 2-2 Reaction/Process Types by Chemical Category for a Sampling of Organic Chemicals

Generic Process	Ethers		Halocarbons			Hydrocarbons					Ke-tones	Ni-trile
	Bis-1 2 Chloroisopropyl Ether	Ethylene Glycol Monomethyl Ether	Epichlorohydrin	Methyl Bromide	1 1,1-Trichloroethane	Butadiene	Hexane	Isoamylene	Styrene	Xylenes	Acetone	Acetonitrile
Alkoxylation		•										
Condensation	•											
Halogenation			•		•							
Oxidation												
Polymerization												
Hydrolysis												
Hydrogenation												
Esterification												
Pyrolysis								•		•	•	
Alkylation									•			
Dehydrogenation						•			•			
Amination (Ammonolysis)												
Nitration												
Sulfonation												
Ammoxidation												•
Carbonylation												
Hydrohalogenation				•								
Dehydration												
Dehydrohalogenation			•									
Oxyhalogenation					•							
Catalytic Cracking							•					
Hydrodealkylation										•		
Phosgenation												
Extraction						•		•				
Distillation						•		•				
Other											•	
Hydration												

Exhibit 2-2 Reaction/Process Types by Chemical Category for a Sampling of Organic Chemicals (cont)

Generic Process	Nitro-Carbon	Phenol	Salt	Misc		Acid	Alcohols		Alde-hyde	Amine	Amide	Anhy-drides	Ester
	Nitrobenzene	p Aminophenol	Sodium Benzoate	Dichlorodiphenyl Sulfone	Methylene Diphenyl Diisocyanate	Sulfonic Acid	n Butanol	1,6-Hexanediol	Benzaldehyde	Hydroxylamine	Formamide	Tetrachloroprophthalic Anhydride	Dimethyl Terephthalate
Alkoxylation													
Condensation					•								
Halogenation												•	
Oxidation			•					•	•			•	•
Polymerization													
Hydrolysis										•			
Hydrogenation		•					•	•					
Esterification								•					•
Pyrolysis													
Alkylation													
Dehydrogenation													
Amination (Ammonolysis)											•		
Nitration	•												
Sulfonation				•									
Ammoxidation													
Carbonylation						•			•				
Hydrohalogenation													
Dehydration												•	
Dehydrohalogenation													
Oxyhalogenation													
Catalytic Cracking													
Hydrodealkylation													
Phosgenation					•								
Extraction													
Distillation													
Other			•	•									
Hydration							•						

The separation technology employed depends on many factors including the phases of the substances being separated, the number of components in the mixture, and whether recovery of by-products is important Numerous techniques such as distillation, extraction, filtration, and settling can be used singly or in combination to accomplish separations Distillation is the process of separating the various constituents of a liquid mixture by partially vaporizing the mixture and recovering the vapor and the residue separately Extraction is a process by which constituents are separated and distributed from one medium into another Filtration is the separation of a fluid-solids mixture by passing most of the fluid through a porous barrier which captures most of the solid particles while allowing the fluid to flow through the barrier Settling is the process by which heavier solid particles come to rest at the bottom of a container while lighter particles remain above them

Relatively few organic chemical manufacturing facilities are single product/process plants Additionally, many process units are designed so that production levels of related products can be varied over wide ranges This flexibility is required to accommodate variations in feedstock and product prices which can change the production rate and processes used, even on a short-term (less than a year) basis

The type of reaction process used to manufacture chemicals depends on the intended product, however, several types of reactions are common polymerization, oxidation, and addition Polymerization is a chemical reaction usually carried out with a catalyst, heat or light (often under high pressure) in which a large number of relatively simple molecules combine to form a chain-like macromolecule Oxidation, in the strict sense, means combining oxygen chemically with another substance although this name is also applied to reactions where electrons are transferred Addition covers a wide range of reactions where a double or triple bond is broken and a component added to the structure Alkylation can be considered an addition, as can some oxidation reactions

2 3 2 Four Specific Industrial Organic Chemicals

This profile examines the reactions of four high-volume chemicals (ethylene, propylene, benzene and vinyl chloride) chosen to illustrate the use of typical chemical feedstocks based on several factors, including the quantity of chemical produced, and the health and environmental impacts of the chemical Ethylene, propylene, and benzene are all primary building blocks and their reaction products are used to produce still other chemicals Vinyl chloride is an important tertiary building block

The four chemicals described below illustrate several key points First, primary building blocks are typically used in more reactions than the building blocks further down the chain Second, most feedstocks can participate in more than one reaction and third, there is typically more than one reaction route to an end-product The end-products of all of these chemicals can be used in numerous commercial applications

2 3 2 1 Ethylene The major uses for ethylene are in the synthesis of polymers (polyethylene) and in ethylene dichloride, a precursor to vinyl chloride Other important products are ethylene oxide (a precursor to ethylene glycol) and ethylbenzene (a precursor to styrene) While ethylene itself is not generally considered a health threat, several of its derivatives, such as ethylene oxide and vinyl chloride, have been shown to cause cancer The manufacturing processes that use ethylene as a feedstock are summarized in Exhibit 2-3 along with reaction conditions and components

Exhibit 2-3 Manufacturing Processes Using Ethylene

Process	Target Product	Process Conditions			Reaction Components	Other Characteristics
		Pressure (MPa)	Temp (°C)	Catalyst		
Polymerization	Low density polyethylene (LDPE)	60 350	350		Oxygen or peroxide	
	High density polyethylene	0 1 20	50 300	Molybdenum Chromium oxide		
	Polyethylene	Low		Aluminum alkyls Titanium oxide		
Oxidation	Ethylene oxide	1-2	250 300	Silver	1 2 Dichloro ethane oxygen	60% is converted to ethylene glycol using an acid catalyst
	Acetaldehyde	0 3	120-130	Copper chloride/ palladium chloride	Oxygen	Vapor phase
	Vinyl acetate	0 4 1	170 200	Palladium	Acetic acid	
Addition Halogenation/ hydrohalogen ation	Ethylene dichloride		60	Iron aluminum copper or antimony chlorides	Chlorine	Feedstock for vinyl chloride and trichloroethylene and tetrachloroethylene
	Ethyl chloride	0 3-0 5		Aluminum or iron chlorides	HCl	Precursor of styrene
Alkylation	Ethylbenzene			Aluminum iron and boron chlorides	Benzene	
Hydroformation	Propionaldehyde	4 35	60 200	Cobalt	Synthesis gas (carbon monoxide and hydrogen)	

2 3 2 2 Propylene Propylene's primary products are polypropylene, acrylonitrile, propylene oxide, and isopropyl alcohol Acrylonitrile and propylene oxide have both been shown to cause cancer, while propylene itself is not generally considered a health threat The important propylene reactions are shown in Exhibit 2-4 The products of the reactions are the feedstocks for numerous additional products

Exhibit 2-4 Manufacturing Processes Using Propylene

Process	Target Product	Process Conditions			Reaction Components	Other Characteristics
		Pressure (MPa)	Temp (°C)	Catalyst		
Polymerization	Polypropylene			Aluminum alkyls/ Titanium oxide		
Oxidation	Acrylonitrile		400	Phosphomolybdate	Ammonia Oxygen	Commercially valuable by products are acetonitrile and hydrogen cyanide
	Propylene oxide				Oxygen Ethylbenzene	Commercially valuable by product is *tert*-butyl alcohol
Addition Chlorohydrination	Propelyene oxide	25	37	Tungsten	Hypochlorous acid	
Hydrolysis	Isopropyl alcohol		267		Water	

2 3 2.3 Benzene Benzene is an important intermediate in the manufacture of industrial chemicals Exhibit 2-5 summarizes the primary benzene reactions The products are frequently feedstocks in the synthesis of additional chemicals Benzene is classified as a human carcinogen in the United States

Exhibit 2-5 Manufacturing Processes Using Benzene

Process	Target Product	Process Conditions			Reaction Components	Other Characteristics
		Pressure (MPa)	Temp (°C)	Catalyst		
Oxidation	Phenol	0 6	90 100		Cumene oxygen	Most important phenol synthesis
	Maleic anhydride	0 1-0 2	350-400	Vanadium oxide	Butane oxygen	
	Styrene	0 1	580-590	Iron oxide	Ethylenebenzene	
Addition Alkylation	Ethylbenzene	0 2-0 4	125-140	Aluminum chloride	Benzene ethylene	Precursor to styrene
	Ethylbenzene	2 0	420-430	Zeolite	Benzene ethylene	Precursor to styrene
	Cumene	0 3 1 0	250-350	Phosphoric acid/silicate	Benzene propylene	
	2 6 Xylenol	0 1-0 2	300-400	Aluminum oxide	Phenol methanol	
Hydrogenation	Cyclohexanone	0 1	140-170	Palladium	Phenol hydrogen	
	Cyclohexanol	1 0 2 0	120-200	Nickel/silicon oxide and aluminum oxide	Phenol hydrogen	
	Cyclohexane	2 0 5 0	150 200	Nickel	Benzene hydrogen	
	Aniline	0 18	270	Copper	Nitrobenzene hydrogen	
Nitration	Nitrobenzene	0 1	60		Benzene sulfuric acid nitric acid	
Sulfonation	Surfactants	0 1	40 50		Alkylbenzene/sulfur trioxide	
Polymerization	Polyvinylchloride		50	Peroxides		
Substitution at the carbon chloride bond	Vinyl acetates alcholates vinyl esters and vinyl ethers			Palladium	Alkyl halides	
Addition	Various halogen addition products					

2 3 2 4 Vinyl Chloride Vinyl chloride polymers are the primary end use of vinyl chloride but various vinyl ethers, esters, and halogen products can also be made as shown in Exhibit 2-6

Exhibit 2-6 Manufacturing Processes Using Vinyl Chloride

Process	Target Product	Process Conditions			Reaction Components	Other Characteristics
		Pressure (MPa)	Temp (°C)	Catalyst		
Polymerization	Polyvinylchloride		50	Peroxides		
Substitution at the carbon chloride bond	Vinyl acetates alcholates vinyl esters and vinyl ethers			Palladium	Alkyl halides	
Addition	Various halogen addition products					

2 3 3 Raw Material Inputs and Pollution Outputs in the Production Line

Industrial organic chemical manufacturers use and generate both large numbers and quantities of chemicals The industry emits chemicals to all media including air (through both fugitive and direct emissions), water (direct discharge and runoff) and land The types of pollutants a single facility will release depend on the feedstocks, processes, equipment in use and maintenance practices These can vary from hour to hour and can also vary with the part of the process that is underway For example, for batch reactions in a closed vessel, the chemicals are more likely to be emitted at the beginning and end of a reaction step (associated with vessel loading and product transfer operations), than during the reaction The potential sources of pollutant outputs by media are shown in Exhibit 2-7

Exhibit 2-7 Potential Releases During Organic Chemical Manufacturing

Media	Potential Sources of Emissions
Air	Point source emissions stack, vent (e g laboratory hood, distillation unit, reactor storage tank vent) material loading/unloading operations (including rail cars tank trucks and marine vessels) Fugitive emissions pumps valves flanges, sample collection mechanical seals relief devices tanks Secondary emissions waste and wastewater treatment units cooling tower process discharge system sump spill/leak areas
Liquid Wastes (organic or aqueous)	Equipment wash solvent/water lab samples surplus chemicals product washes/purifications seal flushes scrubber blowdown cooling water steam jets vacuum pumps leaks spills spent/used solvents housekeeping (pad washdown) waste oils/lubricants from maintenance
Solid Wastes	Spent catalysts spent filters sludges wastewater treatment biological sludge contaminated soil old equipment/insulation packaging material reaction by-products spent carbon/resins drying aids
Ground Water Contamination	Unlined ditches, process trenches sumps, pumps/valves/fittings wastewater treatment ponds product storage areas tanks and tank farms aboveground and underground piping loading/unloading areas/racks manufacturing maintenance facilities

2 4 Summary of Health and Toxicity Effects of Selected Organic Chemicals

2 4 1 Ammonia

Toxicity Anhydrous ammonia is irritating to the skin, eyes, nose, throat, and upper respiratory system

Ecologically, ammonia is a source of nitrogen (an essential element for aquatic plant growth), and may therefore contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters In addition, aqueous ammonia is moderately toxic to aquatic organisms

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Ammonia combines with sulfate ions in the atmosphere and is washed out by rainfall, resulting in rapid return of ammonia to the soil and surface waters

Ammonia is a central compound in the environmental cycling of nitrogen Ammonia in lakes, rivers, and streams is converted to nitrate

Physical Properties Ammonia is a corrosive and severely irritating gas with a pungent odor

2 4 2 Nitric Acid

Toxicity The toxicity of nitric acid is related to its potent corrosivity as an acid, with ulceration of all membranes and tissues with which it comes in contact Concentrated nitric acid causes

immediate opacification and blindness of the cornea when it comes in contact with the eye Inhalation of concentrated nitric acid causes severe, sometimes fatal, corrosion of the respiratory tract Ingestion of nitric acid leads to gastric hemorrhaging, nausea, and vomiting Circulatory shock is often the immediate cause of death due to nitric acid exposure Damage to the respiratory system may be delayed for months, and even years Populations at increased risk from nitric acid exposure include people with pre-existing skin, eye, or cardiopulmonary disorders

Ecologically, gaseous nitric acid is a component of acid rain Acid rain causes serious and cumulative damage to surface waters and aquatic and terrestrial organisms by decreasing water and soil pH levels Nitric acid in rainwater acts as a topical source of nitrogen, preventing "hardening off" of evergreen foliage and increasing frost damage to perennial plants in temperate regions Nitric acid also acts as an available nitrogen source in surface water, stimulating plankton and aquatic weed growth

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Nitric acid is mainly transported in the atmosphere as nitric acid vapors and in water as dissociated nitrate and hydrogen ions In soil, nitric acid reacts with minerals such as calcium and magnesium, becoming neutralized, and at the same time decreasing soil "buffering capacity" against changes in pH levels

Nitric acid leaches readily to groundwater, where it decreases the pH of the affected groundwater In the winter, gaseous nitric acid is incorporated into snow, causing surges of acid during spring snow melt Forested areas are strong sinks for nitric acid, incorporating the nitrate ions into plant tissues

2 4 3 Methanol

Toxicity Methanol is readily absorbed from the gastrointestinal tract and the respiratory tract, and is toxic to humans in moderate to high doses In the body, methanol is converted into formaldehyde and formic acid Methanol is excreted as formic acid Observed toxic effects at high dose levels generally include central nervous system damage and blindness Long-term exposure to high levels of methanol via inhalation cause liver and blood damage in animals

Ecologically, methanol is expected to have low toxicity to aquatic organisms Concentrations lethal to half the organisms of a test population are expected to exceed one milligram (mg) methanol per liter water Methanol is not likely to persist in water or to bioaccumulate in aquatic organisms

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Liquid methanol is likely to evaporate when left exposed Methanol reacts in air to produce formaldehyde which contributes to the formation of air pollutants In the atmosphere it can react with other atmospheric chemicals or be washed out by rain Methanol is readily degraded by microorganisms in soils and surface waters

Physical Properties Methanol is highly flammable

2 4 4 Ethylene Glycol

Sources Ethylene glycol is used as an antifreeze, heat transfer agent and solvent in industrial organic chemical facilities

Toxicity Long-term inhalation exposure to low levels of ethylene glycol may cause throat irritation, mild headache and backache Exposure to higher concentrations may lead to unconsciousness Liquid ethylene glycol is irritating to the eyes and skin

Toxic effects from ingestion of ethylene glycol include damage to the central nervous system and kidneys, intoxication, conjunctivitis, nausea and vomiting, abdominal pain, weakness, low blood oxygen, tremors, convulsions, respiratory failure, and coma Renal failure due to ethylene glycol poisoning can lead to death

Environmental Fate Ethylene glycol readily biodegrades in water No data are available that report its fate in soils, however, biodegradation is probably the dominant removal mechanism Should ethylene glycol leach into the groundwater, biodegradation may occur

Ethylene glycol in water is not expected to bioconcentrate in aquatic organisms, adsorb to sediments or volatilize Atmospheric ethylene glycol degrades rapidly in the presence of hydroxyl radicals

2 4 5 Acetone

Toxicity Acetone is irritating to the eyes, nose, and throat Symptoms of exposure to large quantities of acetone may include headache, unsteadiness, confusion, lassitude, drowsiness, vomiting, and respiratory depression

Reactions of acetone (see environmental fate) in the lower atmosphere contribute to the formation of ground-level ozone Ozone (a major component of urban smog) can affect the respiratory system, especially in sensitive individuals such as asthmatics or allergy sufferers

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate If released into water, acetone will be degraded by microorganisms or will evaporate into the atmosphere Degradation by microorganisms will be the primary removal mechanism

Acetone is highly volatile, and once it reaches the troposphere (lower atmosphere), it will react with other gases, contributing to the formation of ground-level ozone and other air pollutants

Physical Properties Acetone is a volatile and flammable organic chemical

2 5 Pollution Prevention Opportunities

This section provides both general and process-specific descriptions of some pollution prevention advances that have been implemented within the organic chemical industry While the list is not exhaustive, it does provide core information that can be used as the starting point for facilities interested in beginning their own pollution prevention projects

This section provides summary information from activities that may be, or are being implemented bv this sector When possible, information is provided that gives the context in which the technique can be effectively used Please note that the activities described in this section do not necessarily apply to all facilities that fall within this sector Facility-specific conditions must be carefully considered when pollution prevention options are evaluated, and the full impacts of the change must examine how each option affects air, land, and water pollutant releases

Using pollution prevention techniques which prevent the release or generation of pollution in the first place have several advantages over end-of-pipe waste treatment technologies The table below lists the direct and indirect benefits that could result

Exhibit 2-8 Pollution Prevention Activities Can Reduce Costs

Direct Benefits
• Reduced waste treatment costs
Reduced capital and operating costs for waste treatment facilities
Reduced off site treatment and disposal costs
Reduced manufacturing costs due to improved yields
Income or savings from sale or reuse of wastes
Reduced environmental compliance costs (e g fines shutdowns)
Reduced or eliminated inventories or spills
Reduced secondary emissions from waste treatment facilities
Retained sales (production threatened by poor environmental performance or sales)
Indirect Benefits
Reduced likelihood of future costs from
- Remediation
Legal liabilities
Complying with future regulations
Use of emission offsets (internal and external)
Improved community relations
Increase environmental awareness by plant personnel and management
Reduced societal costs
• Improved public health

Pollution prevention can be carried out at any stage of the development of a process In general, changes made at the research and development (R&D) stage will have the greatest impact, however, changes in the process design and operating practices can also yield significant results

In the R&D stage, all possible reaction pathways for producing the desired product can be examined These can then be evaluated in light of yield, undesirable by-products, and their health and environmental impacts

Because of the large investment in current technology, and the lifetime of capital equipment, pollution prevention at the earliest stages is unlikely unless a company undertakes the design of a new production line or facility There are, however, more numerous pollution prevention opportunities that can be realized by modifying current processes and equipment

2 5 1 Opportunities from Process/Product Modifications

This section can be used as a diagnostic tool for identifying common pollution-creating problems that organic chemical processing facilities may experience Suggested solutions to prevent or reduce pollution loads, based on the latest data, follow each potential problem

2 5 1 1 By-products and Co-products

Quantity and Quality

Problem Process inefficiencies result in the generation of undesired by-products and co-products Inefficiencies will require larger volumes of raw materials and result in additional secondary products Inefficiencies can also increase fugitive emissions and wastes generated through material handling
Solution Increase product yield to reduce by-product and co-product generation and raw material requirements

Uses and Outlets

Problem By-products and co-products are not fully utilized, generating material or waste that must be managed
Solution Identify uses and develop a sales outlet Collect information necessary to firm up a purchase commitment such as minimum quality criteria, maximum impurity levels that can be tolerated, and performance criteria

2 5 1 2 Catalysts

Composition

Problem The presence of heavy metals in catalysts can result in contaminated process wastewater from catalyst handling and separation These wastes may require special treatment and disposal procedures or facilities Heavy metals can be inhibitory or toxic to biological wastewater treatment units Sludge from wastewater treatment units may be classified as hazardous due to heavy metals content Heavy metals generally exhibit low toxicity thresholds in aquatic environments and may bioaccumulate
Solution Catalysts comprised of noble metals, because of their cost, are generally recycled by both on-site and off-site reclaimers

Preparation and Handling

Problem Emissions or effluents are generated with catalyst activation or regeneration
Solution Obtain catalyst in the active form Provide in situ activation with appropriate processing/activation facilities

Problem Catalyst attrition and carryover into product requires de-ashing facilities which are a likely source of wastewater and solid waste
Solution Develop a more robust catalyst or support

Problem Catalyst is spent and needs to be replaced
Solution In situ regeneration eliminates unloading/loading emissions and effluents versus off-site regeneration or disposal

Problem Pyrophoric catalyst needs to be kept wet, resulting in liquid contaminated with metals
Solution Use a non-pyrophoric catalyst Minimize amount of water required to handle and store safely

Problem Short catalyst life
Solution Study and identify catalyst deactivitation mechanisms Avoid conditions which promote thermal or chemical deactivation By extending catalyst life, emissions and effluents associated with catalyst handling and regeneration can be reduced

Effectiveness

Problem Catalyzed reaction has by-product formation, incomplete conversion and less-than-perfect yield
Solution Reduce catalyst consumption with a more active form A higher concentration of active ingredient or increased surface area can reduce catalyst loadings Use a more selective catalyst which will reduce the yield of undesired by-products Improve reactor mixing/contacting to increase catalyst effectiveness

Problem Catalyzed reaction has by-product formation, incomplete conversion and less-than perfect yield
Solution Develop a thorough understanding of reaction to allow optimization of reactor design Include in the optimization, catalyst consumption and by-product yield

2 5 1 3 Intermediate Products

Quantity and Quality

Problem Intermediate reaction products or chemical species, including trace levels of toxic constituents, may contribute to process waste under both normal and upset conditions
Solution Modify reaction sequence to reduce amount or change composition of intermediates

Problem Intermediates may contain toxic constituents or have characteristics that are harmful to the environment

Solution Modify reaction sequence to change intermediate properties Use equipment design and process control to reduce releases

2 5 1 4 Process Conditions/Configuration

Temperature

Problem High heat exchange tube temperatures cause thermal cracking/decomposition of many chemicals These lower molecular weight by-products are a source of "light ends" and fugitive emissions High localized temperature gives rise to polymerization of reactive monomers, resulting in "heavies" or "tars " such materials can foul heat exchange equipment or plug fixed-bed reactors, thereby requiring costly equipment cleaning and production outage
Solution Select operating temperatures at or near ambient temperature whenever possible Use lower pressure steam to lower temperatures Use intermediate exchangers to avoid contact with furnace tubes and walls Use staged heating to minimize product degradation and unwanted side reactions Use superheat of high-pressure steam in place of furnace Monitor exchanger fouling to correlate process conditions which increase fouling, avoid conditions which rapidly foul exchangers Use online tube cleaning technologies to keep tube surfaces clean to increase heat transfer Use scraped wall exchangers in viscous service Use falling film reboiler, pumped recirculation reboiler or high-flux tubes

Problem Higher operating temperatures imply "heat input" usually via combustion which generates emissions
Solution Explore heat integration opportunities (e g , use waste heat to preheat materials and reduce the amount of combustion required)

Problem Heat sources such as furnaces and boilers are a source of combustion emissions
Solution Use thermocompressors to upgrade low-pressure steam to avoid the need for additional boilers and furnaces If possible, cool materials before sending to storage

Problem Vapor pressure increases with increasing temperature Loading/unloading, tankage and fugitive emissions generally increase with increasing vapor pressure
Solution Use hot process streams to reheat feeds Add vent condensers to recover vapors in storage tanks or process Add closed dome loading with vapor recovery condensers

Problem Water solubility of most chemicals increases with increasing temperature
Solution Use lower temperature (vacuum processing)

Pressure

Problem Fugitive emissions from equipment
Solution Equipment operating in vacuum service is not a source of fugitives, however, leaks into the process require control when system is degassed

Problem Seal leakage potential due to pressure differential
Solution Minimize operating pressure

Problem Gas solubility increases with higher pressures
Solution Determine whether gases can be recovered, compressed, and reused or require controls

Corrosive Environment

Problem Material contamination occurs from corrosion products Equipment failures result in spills, leaks and increased maintenance costs
Solution Improve metallurgy or provide coating or lining Neutralize corrosivity of materials contacting equipment Use corrosion inhibitors

Problem Increased waste generation due to addition of corrosion inhibitors or neutralization
Solution Improve metallurgy or provide coating or lining or operate in a less corrosive environment

Batch vs Continuous Operations

Problem Vent gas lost during batch fill
Solution Equalize reactor and storage tank vent lines Recover vapors through condenser, adsorber, etc

Problem Waste generated by cleaning/purging of process equipment between production batches
Solution Use materials with low viscosity Minimize equipment roughness

Problem Process inefficiencies yield lower yield and increase emissions
Solution Optimize product manufacturing sequence to minimize washing operations and cross-contamination of subsequent batches

Problem Continuous process fugitive emissions and waste increase over time due to equipment failure through a lack of maintenance between turnarounds
Solution Sequence addition of reactants and reagents to optimize yields and lower emissions Design facility to readily allow maintenance so as to avoid unexpected equipment failure and resultant release

Process Operation/Design

Problem Numerous processing steps create wastes and opportunities for errors
Solution Keep it simple Make sure all operations are necessary More operations and complexity only tend to increase potential emission and waste sources

Problem Non-reactant materials (solvents, absorbants, etc) create wastes Each chemical (including water) employed within the process introduces additional potential waste sources, the composition of generated wastes also tends to become more complex
Solution Evaluate unit operation or technologies (e g , separation) that do not require the addition of solvents or other non-reactant chemicals

Problem High conversion with low yield results in wastes
Solution Recycle operations generally improve overall use of raw materials and chemicals, thereby

both increasing the yield of desired products while at the same time reducing the generation of wastes A case-in-point is to operate at a lower conversion per reaction cycle by reducing catalyst consumption, temperature, or residence time Many times, this can result in a higher selectivity to desired products The net effect upon recycle of unreacted reagents is an increase in product yield while at the same time reducing the quantities of spent catalyst and less desirable by-products

Problem Non-regenerative treatment systems result in increased waste versus regenerative systems
Solution Regenerative fixed bed treating or desiccant operation (e g , aluminum oxide, silica activated carbon, molecular sieves, etc) will generate less quantities of solid or liquid waste than non-regenerative units (e g , calcium chloride or activated clay) With regenerative units though, emissions during bed activation and regeneration can be significant Further, side reactions during activation/regeneration can give rise to problematic pollutants

2 5 1 5 Product

Process Chemistry

Problem Insufficient R&D of alternative reaction pathways may miss pollution opportunities such as waste reduction or eliminating a hazardous constituent
Solution R&D during process conception and laboratory studies should thoroughly investigate alternatives in process chemistry that affect pollution prevention

Product Formulation

Problem Product based on end-use performance may have undesirable environmental impacts or use raw materials or components that generate excessive or hazardous wastes
Solution Reformulate products by substituting different material or using a mixture of individual chemicals that meet end-use performance specifications

2 5 1 6 Raw Materials

Purity

Problem Impurities may produce unwanted by-products and waste Toxic impurities, even in trace amounts, can make a waste hazardous and therefore subject to strict and costly regulation
Solution Use higher purity materials Purify materials before use and reuse if practical Use inhibitors to prevent side reactions

Problem Excessive impurities may require more processing and equipment to meet product specifications, increasing costs and potential for fugitive emissions, leaks, and spills
Solution Achieve balance between feed purity, processing steps, product quality and waste generation

Problem Specifying a purity greater than needed by the process increases costs and can result in more waste generation by the supplier
Solution Specify a purity no greater than what the process needs

Problem Impurities in clean air can increase inert purges
Solution Use pure oxygen

Problem Impurities may poison catalyst prematurely resulting in increased wastes due to yield loss and more frequent catalyst replacement
Solution Install guard beds to protect catalysts

Vapor Pressure

Problem Higher vapor pressures increase fugitive emissions in material handling and storage
Solution Use material with lower vapor pressure

Problem High vapor pressure with low odor threshold materials can cause nuisance odors
Solution Use materials with lower vapor pressure and higher odor threshold

Water Solubility

Problem Toxic or non-biodegradable materials that are water soluble may affect wastewater treatment operation, efficiency, and cost
Solution Use less toxic or more biodegradable materials

Problem Higher solubility may increase potential for surface and groundwater contamination and may require more careful spill prevention, containment, and cleanup plans
Solution Use less soluble materials

Problem Higher solubility may increase potential for storm water contamination in open areas
Solution Use less soluble materials Prevent direct contact with storm water by diking or covering areas

Problem Process wastewater associated with water washing or hydrocarbon/water phase separation will be impacted by containment solubility in water Appropriate wastewater treatment will be impacted
Solution Minimize water usage Reuse wash water Determine optimum process conditions for phase separation Evaluate alternative separation technologies (coalescers, membranes, distillation, etc)

Toxicity

Problem Community and worker safety and health concerns result from routine and non-routine emissions Emissions sources include vents, equipment leaks, wastewater emissions, emergency pressure relief, etc
Solution Use less toxic materials Reduce exposure through equipment design and process control Use systems which are passive for emergency containment of toxic releases

Problem Surges or higher than normal continuous levels of toxic materials can shock or miss wastewater biological treatment systems resulting in possible fines and possible toxicity in the receiving water

Solution Use less toxic material Reduce spills, leaks and upset conditions through equipment and process control Consider effect of chemicals on biological treatment, provide unit pretreatment or diversion capacity to remove toxicity Install surge capacity for flow and concentration equalization

Form of Supply

Problem Small containers increase shipping frequency which increases chances of material releases and waste residues from shipping containers (including wash waters)
Solution Use bulk supply, ship by pipeline, or use "jumbo" drums or sacks In some cases, product may be shipped out in the same containers the material supply was shipped in without washing

Problem Nonreturnable containers may increase waste
Solution Use returnable shipping containers or drums

Handling and Storage

Problem Physical state (solid, liquid, gaseous) may raise unique environmental, safety, and health issues with unloading operations and transfer to process equipment
Solution Use equipment and controls appropriate to the type of materials to control releases

Problem Large inventories can lead to spills, inherent safety issues and material expiration
Solution Minimize inventory by utilizing just-in-time delivery

2 5 1 7 Waste Streams

Quantity and Quality

Problem Characteristics and sources of waste streams are unknown
Solution Document sources and quantities of waste streams prior to pollution prevention assessment

Problem Wastes are generated as part of the process
Solution Determine what changes in process conditions would lower waste generation of toxicity Determine if wastes can be recycled back into the process

Composition

Problem Hazardous or toxic constituents are found in waste streams Examples are sulfides, heavy metals, halogenated hydrocarbons, and polynuclear aromatics
Solution Evaluate whether different process conditions, routes, or reagent chemicals (e g , solvent catalysts) can be substituted or changed to reduce or eliminate hazardous or toxic compounds

Properties

Problem Environmental fate and waste properties are not known or understood
Solution Evaluate waste characteristics using the following type properties corrosivity, ignitability, reactivity, BTU content (energy recovery), biodegradability, aquatic toxicity, and

bioaccumulation potential of the waste and of its degradable products, and whether it is a solid liquid, or gas

Disposal

Problem Ability to treat and manage hazardous and toxic waste unknown or limited
Solution Consider and evaluate all on-site and off-site recycle, reuse, treatment, and disposal options available Determine availability of facilities to treat or manage wastes generated

Exhibit 2-9 Pollution Preventing Equipment Modifications

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Compressors blowers fans	▪ Shaft seal leaks piston rod seal leaks and vent streams	▪ Seal-less designs (diaphragmatic hermetic or magnetics) ▪ Design for low emissions (internal balancing double inlet gland eductors) ▪ Shaft seal designs (carbon rings double mechanical seals buffered seals) ▪ Double seal with barrier fluid vented to control device	▪ Preventive maintenance program
Concrete pads floors sumps	▪ Leaks to groundwater	▪ Water stops ▪ Embedded metal plates ▪ Epoxy sealing ▪ Other impervious sealing	▪ Reduce unnecessary purges transfers and sampling ▪ Use drip pans where necessary

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Controls	▪ Shutdowns and start-ups generate waste and releases	▪ Improve on-line controls ▪ On line instrumentation ▪ Automatic start up and shutdown ▪ On line vibration analysis ▪ Use consensus systems (e g shutdown trip requires two out of three affirmative responses)	▪ Continuous versus batch ▪ Optimize on line run time ▪ Optimize shutdown interlock inspection frequency ▪ Identify safety and environment critical instruments and equipment
Distillation	▪ Impurities remain in process streams ▪ Large amounts of contaminated water condensate from stream stripping	▪ Increase reflux ratio ▪ Add section to column ▪ Column intervals ▪ Change feed tray ▪ Insulate to prevent heat loss ▪ Preheat column feed ▪ Increase vapor line size to lower pressure drop ▪ Use reboilers or inert gas stripping agents	▪ Change column operating conditions reflux ratio - feed tray temperature - pressure etc ▪ Clean column to reduce fouling ▪ Use higher temperature steam

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
General manufacturing equipment areas	▪ Contaminated rainwater	▪ Provide roof over process facilities	▪ Return samples to process
		▪ Segregate process discharge system from storm drainage system (diking)	▪ Monitor storm water discharge
		▪ Hard-pipe process streams to process discharge system	
	▪ Contaminated sprinkler and fire water	▪ Seal floors	
		▪ Drain to sump	
		▪ Route to waste treatment	
	▪ Leaks and emissions during cleaning	▪ Design for cleaning	▪ Use drip pans for maintenance activities
		▪ Design for minimum rinsing	▪ Rinse to sump
		▪ Design for minimum sludge	▪ Reuse cleaning solutions
		▪ Provide vapor enclosure	
		▪ Drain to process	

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Heat exchangers	▪ Increased waste due to high localized temperatures	▪ Use intermediate exchangers to avoid contact with furnace tubes and walls ▪ Use staged heating to minimize product degradation and unwanted side reactions (waste heat > > low pressure steam > > high pressure steam) ▪ Use scraped wall exchangers in viscous service ▪ Using falling film reboiler piped recirculation reboiler or high-flux tubes ▪ Use lowest pressure steam possible	▪ Select operating temperatures at or near ambient temperature when ever possible These are generally most desirable from a pollution prevention standpoint ▪ Use lower pressure steam to lower temperatures ▪ Monitor exchanger fouling to correlate process conditions which increase fouling avoid conditions which rapidly foul exchangers ▪ Use on line tube cleaning techniques to keep tube surfaces clean
	▪ Contaminated materials due to tubes leaking at tube sheets	▪ Use welded tubes or double tube sheets with inert purge Mount vertically	▪ Monitor for leaks
	▪ Furnace emissions	▪ Use super heat of high pressure steam in place of a furnace	

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Piping	▪ Leaks to groundwater/ fugitive emissions	▪ Design equipment layout so as to minimize pipe run length ▪ Eliminate underground piping or design for cathodic protection if necessary to install piping underground ▪ Use welded fittings ▪ Reduce number of flanges and valves ▪ Use all welded pipe ▪ Use secondary containment ▪ Use spiral-wound gaskets ▪ Use plugs and double valves for open end lines ▪ Change metallurgy ▪ Use lined pipe	▪ Monitor for corrosion and erosion ▪ Paint to prevent external corrosion
	▪ Releases when cleaning or purging lines	▪ Use pigs for cleaning ▪ Slope to low point drain ▪ Use heat tracing and insulation to prevent freezing ▪ Install equalizer lines	▪ Flush to product storage tank

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Pumps	▪ Fugitive emissions from shaft seal leaks	▪ Mechanical seal in lieu of packing ▪ Double mechanical seal with inert barrier fluid ▪ Double machined seal with barrier fluid vented to control device ▪ Seal-less pump (canned motor magnetic drive) ▪ Vertical pump	▪ Seal installation practices ▪ Monitor for leaks
	▪ Fugitive emissions from shaft seal leaks	▪ Use pressure transfer to eliminate pump	
	▪ Residual heel of liquid during pump maintenance	▪ Low point drain on pump casing	▪ Flush casing to process discharge system for treatment ▪ Increase the mean time between pump failures by selecting proper seal material aligning well reducing pipe induced stress maintaining seal lubrication
	▪ Injection of seal flush fluid into process stream	▪ Use double mechanical seal with inert barrier fluid where practical	

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Reactors	▪ Poor conversion or performance due to inadequate mixing	▪ Static mixing ▪ Add baffles ▪ Change impellers ▪ Add horsepower ▪ Add distributor	▪ Add ingredients with optimum sequence ▪ Allow proper head space in reactor to enhance vortex effect
	▪ Waste by product formation	▪ Provide separate reactor for converting recycle streams to usable products	▪ Optimize reaction conditions (temperature pressure etc)
Relief Valve	▪ Leaks	▪ Provide upstream rupture disc	
	▪ Fugitive emissions	▪ Vent to control or recovery device	▪ Monitor for leaks and for control efficiency
	▪ Discharge to environment from over pressure	▪ Pump discharges to suction of pump ▪ Thermal relief to tanks ▪ Avoid discharge to roof areas to prevent contamination of rainwater	▪ Monitor for leaks
	▪ Frequent relief	▪ Use pilot operated relief valve ▪ Increase margin between design and operating pressure	▪ Reduce operating pressure ▪ Review system performance

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Sampling	▪ Waste generation due to sampling (disposal containers leaks fugitives etc)	▪ In line in situ analyzers ▪ System for return to process ▪ Closed loop ▪ Drain to sump	▪ Reduce number and size of samples required ▪ Sample at the lowest possible temperature ▪ Cool before sampling
Tanks	▪ Tank breathing and working losses	▪ Cool materials before storage ▪ Insulate tanks ▪ Vent to control device (flare condenser etc) ▪ Vapor balancing ▪ Floating roof ▪ Higher design pressure	▪ Optimize storage conditions to reduce losses
	▪ Leak to groundwater	▪ All aboveground (situated so bottom can routinely be checked for leads) ▪ Secondary containment ▪ Improve corrosion resistance	▪ Monitor for leaks and corrosion
	▪ Large waste heel	▪ Design for 100 % de inventory	▪ Recycle to process if practical
Vacuum Systems	▪ Waste discharge from jets	▪ Substitute mechanical vacuum pump ▪ Evaluate using process fluid for powering jet	▪ Monitor for air leaks ▪ Recycle condensate to process

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Valves	▪ Fugitive emissions from leaks	▪ Bellow seals ▪ Reduce number where practical ▪ Special packing sets	▪ Stringent adherence to packing procedures
Vents	▪ Release to environment	▪ Route to control or recovery device	▪ Monitor performance

CHAPTER 3
INORGANIC CHEMICAL PROCESSING[2]

3 1 Introduction

The inorganic chemical industry manufactures over 300 different types of chemicals For the purposes of this manual, the category of inorganic chemicals includes alkalies and chlorine industrial gases (e g , hydrogen, helium, oxygen, nitrogen, etc), inorganic pigments, and some forms of industrial inorganic chemicals

3 2 Product Characterization

3 2 1 Inorganic Chemicals Industry

The inorganic chemical industry manufactures chemicals which are often of a mineral origin, but not of a basic carbon molecular structure Inorganic chemicals are used at some stage in the manufacture of a great variety of other products The industry's products are used as basic chemicals for industrial processes (i e , acids, alkalies, salts, oxidizing agents, industrial gases, and halogens), chemical products to be used in manufacturing products (i e , pigments, dry colors, and alkali metals), and finished products for ultimate consumption (i e , mineral fertilizers, glass, and construction materials) The largest use of inorganic chemicals is as processing aids in the manufacture of chemical and nonchemical products

3 2 2 Chlor-alkali Sector

The chlor-alkali industry produces mainly chlorine, caustic soda (sodium hydroxide), soda ash (sodium carbonate), sodium bicarbonate, potassium hydroxide, and potassium carbonate

Chlorine is used in the manufacturing of organic chemicals including vinyl chloride monomer, ethylene dichloride, glycerine, glycols, chlorinated solvents, and chlorinated methanes Vinyl chloride is used in the production of polyvinyl chloride (PVC) Other major uses are disinfection treatment of water, and the production of hypochlorites

The largest users of caustic soda are the organic chemicals industry and the inorganic chemicals industry The primary uses of caustic soda are in industrial processes, neutralization, and off-gas scrubbing, as a catalyst, and in the production of alumina, propylene oxide, polycarbonate resin, epoxies, synthetic fibers, soaps, detergents, rayon, and cellophane Caustic soda is also used in the production of soaps and cleaning products, and in

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[2] The information in this chapter is derived from the U S Environmental Protection Agency's Office of Compliance Sector Notebook Project, *Profile of the Inorganic Chemical Industry*, September 1995 (document # EPA/310-R-95-012) Readers should refer to that document for a comprehensive set of references and sources Contact your local EP3 Clearinghouse for a copy of the EPA document or for information on how to access it electronically via the Internet

the petroleum and natural gas extraction industry as a drilling fluid

3 3 Industrial Process Description

This section describes the major industrial processes within the inorganic chemical industry, including the materials and equipment used, and the processes employed This discussion also provides a concise description of where wastes may be produced in the process and describes the potential fate (via air, water, and soil pathways) of these waste products

3 3 1 Industrial Processes in the Inorganic Chemical Industry

Chlorine and caustic soda are co-products of electrolysis of saturated aqueous solutions of sodium chloride, NaCl (salt water or brine) In addition, relatively small amounts (by weight) of hydrogen gas are produced in the process The overall chemical reaction is as follows

$$2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + Cl_2 + H_2$$

Energy, in the form of direct current (d-c) electricity, is supplied to drive the reaction The amount of electrical energy required depends on the design of the electrolytic cell, the voltage used, and the concentration of brine used For each ton of chlorine produced, 1 1 tons of sodium hydroxide and 28 kgs of hydrogen are produced

Three types of electrolysis processes are used for the manufacture of chlorine, caustic soda, and hydrogen from brine

- Mercury Cell Process
- Diaphragm Cell Process
- Membrane Cell Process

Each electrolytic cell consists of an anode and cathode in contact with the brine solution The distinguishing feature of each cell type is the method employed to separate and prevent the mixing of the chlorine gas and sodium hydroxide Consequently, each process produces a different purity of chlorine gas and a different concentration of caustic soda The inorganics chemical industry in the U S is moving away from mercury and diaphragm cells and is moving towards the use of membrane cells Membrane cells are a relatively recent development which have fewer adverse effects on the environment and produce a higher quality product at a lower cost than the other methods

Exhibit 3-1 Main Characteristics of the Different Electrolysis Processes

Component	Mercury Cell	Diaphragm Cell	Membrane Cell
Cathode	Mercury flowing over steel	Steel or steel coated with activated nickel	Steel or nickel with a nickel based catalytic coating
Diaphragm/ Membrane	None	Asbestos or polymer modified asbestos	Ion-exchange membrane
Anode	Titanium with RuO_2 or TiO_2 coating (DSA anode)	Titanium with RuO_2 or TiO_2 coating (DSA anode)	Titanium with RuO or TiO coating (DSA anode)
Cathode Product	Sodium amalgam	10-12% NaOH with 15 17% NaCl and H_2	30 33% NaOH and H_2
Decomposer/ Evaporator Product	50% NaOH and H_2 from decomposer	50% NaOH with 1% NaCl and solid salt from evaporator	50% NaOH with very little salt
Electricity Consumption	3 300 kWh per ton Cl_2	2 750 kWh per ton Cl_2	2 100 2 450 kWh per ton NaOH

3 3 1 1 Mercury Cell The mercury cell process consists of slightly inclined steel troughs through which a thin layer of mercury (about three mm) flows over the bottom The cells are operated at 75 to 85°Centigrade (C) and atmospheric pressure The mercury layer serves as the cathode for the process and the saturated brine solution (25 5 percent NaCl by weight) flows through the troughs above the mercury The anodes are usually incorporated into the cell covers and are suspended horizontally in the brine solution The height of the anodes within the brine is adjusted to the optimal height either manually or through an automatic computer controlled system

Electrolytic cell anodes were made of graphite until the late 1960s when anodes of titanium coated with ruthenium oxide (RuO_2) and titanium oxide (TiO_2) were developed The RuO_2 and TiO_2 anodes, termed DSA (dimensionally stable) anodes, are more stable than the graphite anodes (i e , they do not need to be replaced as frequently) and are more energy efficient

The chlorine gas is produced at the anodes where it moves upward through gas extraction slits in the cell covers Sodium ions are absorbed by the mercury layer and the resulting sodium and mercury mixture, called the amalgam, is processed in "decomposer" cells to generate sodium hydroxide and reusable mercury The amalgam entering the decomposer cell has a sodium concentration of approximately 0 2 to 0 5 percent by weight The decomposer consists of a short-circuited electrical cell where graphite serves as the anode and the amalgam serves as the cathode The amalgam and water flowing through the cell come into direct contact with the graphite The hydrolysis of the water on the graphite in the presence of the amalgam results in a strong exothermic reaction generating mercury to be reused in the electrolytic cell, a 50 percent caustic soda solution, and hydrogen gas Mercury cells are operated to maintain a 21 to 22 percent by weight NaCl concentration in the depleted brine leaving the cell The dissolved chlorine is removed from the depleted brine solution, which is then re-saturated with solid salt and purified for further use Some facilities purge small amounts of brine solution

and use new brine as make-up in order to prevent the build up of sulfate impurities in the brine

The mercury process has the advantage over diaphragm and membrane cells in that it produces a pure chlorine gas with no oxygen, and a pure 50 percent caustic soda solution without having to further concentrate a more dilute solution However, mercury cells operate at a higher voltage than diaphragm and membrane cells and, therefore, use more energy The process also requires a very pure brine solution with little or no metal contaminants Furthermore, elaborate precautions must be taken to avoid releases of mercury to the environment

3 3 1 2 Diaphragm Cell In the diaphragm cell process, multiple cells consisting of DSA anode plates and cathodes are mounted vertically and parallel to each other Each cell consists of one anode and cathode pair The cathodes are typically flat hollow steel mesh or perforated steel structures covered with asbestos fibers, which serve as the diaphragm The asbestos fiber structure of the diaphragm prevents the mixing of hydrogen and chlorine by allowing liquid to pass through to the cathode, but not fine bubbles of chlorine gas formed at the anodes The diaphragm also hinders the back-diffusion to the anode of hydroxide (OH^-) ions formed at the cathode The cells are operated at 90 to 95°C and atmospheric pressure Brine flows continuously into the anode chamber and, subsequently, through the diaphragm to the cathode As in the mercury cell process, chlorine gas is formed at the anodes, however, in the diaphragm process, caustic soda solution and hydrogen gas are formed directly at the cathode The chlorine gas is drawn off from above the anodes for further processing The hydrogen gas is drawn off separately from the cathode chambers

Two basic types of diaphragm cells are in use today The first, monopolar cells, have an electrode arrangement in which the anodes and cathodes are arranged in parallel As a result of this configuration, all cells have the same voltage of about three to four volts, up to 200 cells can be constructed in one circuit The second basic type of diaphragm cell is the bipolar cell, in which the anode of one cell is directly connected to the cathode of the next cell unit This type of arrangement minimizes voltage loss between cells, however, since the total voltage across the entire set of cells is the sum of the individual cell voltages, the number of cells per unit is limited To compensate for the reduced anode and cathode surface area in the bipolar configuration, bipolar units tend to be much larger than monopolar units Production of chlorine and caustic soda by the diaphragm process is split approximately equally between monopolar and bipolar systems

Diaphragm cells are operated such that about 50 percent of the input NaCl is decomposed resulting in an effluent mixture of brine and caustic soda solution containing eight to 12 percent NaOH and 12 to 18 percent NaCl by weight This solution is evaporated to 50 percent NaOH by weight at which point all of the salt, except a residual 1 0 to 1 5 percent by weight, precipitates out The salt generated is very pure and is typically used to make more brine Because the brine and caustic soda solution are mixed in a single effluent, a fresh brine solution (no recycled brine) is constantly entering the system The diaphragm cell process does not, therefore, require a brine purge to prevent sulfate build up, or treatment to remove entrained chlorine gas, as in the mercury cell process

Diaphragms are constructed of asbestos because of its chemical and physical stability and because it is a relatively inexpensive and abundant material Diaphragm cells have the advantage of operating at a lower voltage than mercury cells and, therefore, use less electricity In addition, the brine entering a diaphragm cell can be less pure than that required by mercury and membrane cells The chlorine gas produced by the diaphragm process, however, is not pure and must be processed to remove oxygen, water, salt, and sodium hydroxide Another disadvantage of the process is that the caustic soda produced contains chlorides and requires evaporation to bring it to a usable concentration

3 3 1 3 Membrane Cell In the membrane cell process, the anode and cathode are separated by a water-impermeable ion-conducting membrane Brine solution flows through the anode compartment where chlorine gas is generated The sodium ions migrate through the membrane to the cathode compartment which contains flowing caustic soda solution Water is hydrolyzed at the cathode, releasing hydrogen gas and hydroxide (OH) ions The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32 to 35 percent by recirculating the solution before it is discharged from the cell The membrane prevents the migration of chloride ions from the anode compartment to the cathode compartment, therefore, the caustic soda solution produced does not contain salt as in the diaphragm cell process Depleted brine is discharged from the anode compartment and re-saturated with salt

The cathode material used in membrane cells is either stainless steel or nickel The cathodes are often coated with a catalyst that is more stable than the substrate and that increases surface area and electrical conductivity Coating materials include Ni-S, Ni-Al, and Ni-NiO mixtures, as well as mixtures of nickel and platinum group metals Anodes are typically of the DSA type

The most critical components of the membrane cells are the membranes themselves The membranes must remain stable while being exposed to chlorine on one side and a strong caustic solution on the other Furthermore, the membranes must have low electrical resistance, and allow the transport of sodium ions and not chloride ions and reinforcing fabric, and a perfluorocarboxlate polymer all bonded together

Membrane cells can be configured either as monopolar or bipolar As in the case of the diaphragm cell process, the bipolar cells have less voltage loss between the cells than the monopolar cells, however, the number of cells connected together in the same circuit is limited

Membrane cells have the advantages of producing a very pure caustic soda solution and of using less electricity than the mercury and diaphragm processes In addition, the membrane process does not use highly toxic materials such as mercury and asbestos Disadvantages of the membrane process are that the chlorine gas produced must be processed to remove oxygen and water vapor, and the caustic soda produced must be evaporated to increase the concentration Furthermore, the brine entering a membrane cell must be of a very high purity, which often requires costly additional purification steps prior to electrolysis

3 3 2 Auxiliary Processes

3 3 2 1 Brine Purification Approximately 70 percent of the salt used in chlorine gas production is extracted from natural salt deposits, the remainder is evaporated from seawater Salt from natural deposits is either mined in solid form or is leached from the subsurface Leaching involves the injection of freshwater into subterranean salt deposits and pumping out brine solution Brine production from seawater typically occurs by solar evaporation in a series of ponds to concentrate the seawater, precipitate out impurities, and precipitate out solid sodium chloride Regardless of the method used to obtain the salt, it will contain impurities that must be removed before being used in the electrolysis process Impurities primarily consist of calcium, magnesium, barium, iron, aluminum, sulfates, and trace metals Impurities can significantly reduce the efficiency of the electrolytic cells, by precipitating out and subsequently blocking a diaphragm or damaging a membrane depending on the process used Certain trace metals, such as vanadium, reduce the efficiency of mercury cells and cause the production of potentially dangerous amounts of hydrogen gas Removal of impurities accounts for a significant portion of the overall costs of chlor-alkali production, especially in the membrane process

In addition to the dissolved natural impurities, chlorine must be removed from the recycled brine solutions used in mercury and membrane processes Dissolved chlorine gas entering the anode chamber in the brine solution will react with hydroxide ions formed at the cathode to form chlorate which reduces product yields In addition, chlorine gas in the brine solution will cause corrosion of pipes, pumps, and containers during further processing of the brine In a typical chlorine plant, HCl is added to the brine solution leaving the cells to liberate the chlorine gas A vacuum is applied to the solution to collect the chlorine gas for further treatment To further reduce the chlorine levels, sodium sulfite or another reducing agent is added to remove the final traces of chlorine Dechlorinated brine is then re-saturated with solid salt before further treating to remove impurities

Depending on the amount of impurities in the salt and the electrolysis process utilized, different purification steps will be required Brine solution is typically heated before treatment to improve reaction times and precipitation of impurities Calcium carbonate impurities are precipitated out through treatment with sodium carbonate, magnesium, iron, and aluminum are precipitated out through treatment with sodium hydroxide, and sulfates are precipitated out through the addition of calcium chloride or barium carbonate Most trace metals are also precipitated out through these processes Flocculants are sometimes added to the clarifying equipment to improve settling The sludges generated in this process are washed to recover entrained sodium chloride Following the clarification steps, the brine solution is typically passed through sand filters followed by polishing filters The brine passing through these steps will contain less than four parts per million (ppm) calcium and 0 5 ppm magnesium which is sufficient purification for the diaphragm and mercury cell processes For brine to be used in the membrane process, however, requires a combined calcium and magnesium content of less than 20 parts per billion (ppb) Brine for the membrane process is, therefore, passed through ion exchange columns to further remove impurities

3 3 2 2 Chlorine Processing The chlorine gas produced by electrolytic processes is saturated with water vapor Chlorine gas from the diaphragm process also contains liquid

droplets of sodium hydroxide and salt solution The first steps in processing the chlorine to a usable product consists of cooling the chlorine to less than 10°C and then passing it through demisters or electrostatic precipitators to remove water and solids Next the chlorine is passed through packed towers with concentrated sulfuric acid flowing counter currently The water vapor is absorbed by the sulfuric acid and the dry chlorine gas is then passed through demisters to remove sulfuric acid mist If the chlorine is to be liquefied, liquid chlorine is then added to the gas to further purify the chlorine and to prechill it prior to compression Prechilling is primarily carried out to prevent the temperature from reaching the chlorine-steel ignition point during compression

Chlorine gas is either used in gaseous form within the facility, transferred to customers via pipeline, or liquefied for storage or transport Liquid chlorine is of a higher purity than gaseous chlorine and is either used within the facility or is transferred via rail tank car, tank truck, or tank barge

Chlorine liquefaction processes typically liquefy only about 90-95 percent of the chlorine This gas and the chlorine gas left inside tank truck tanks, rail car tanks, or barges after removal of liquid chlorine is impure and must be recovered in a chlorine recovery unit The gas is compressed and cooled using cold water followed by Freon The chilled gas is fed up through a packed column in which carbon tetrachloride flows downward absorbing the chlorine The chlorine-rich carbon tetrachloride is fed to a chlorine stripper in which the chlorine and carbon tetrachloride separate as they are heated The chlorine gas is cooled and scrubbed of carbon tetrachloride using liquid chlorine and the resulting pure chlorine is sent to the chlorine liquefaction system

3 3 2 3 Caustic Soda Processing Caustic soda solution generated from chlor-alkali processes is typically processed to remove impurities and to concentrate it to either a 50 percent or 73 percent water-based solution or to anhydrous caustic soda The caustic soda from the mercury and membrane processes is relatively pure Product from the mercury process requires only filtration to remove mercury droplets The evaporators used to concentrate the caustic soda solution in the diaphragm process are typically multi-stage forced circulation evaporators The evaporators have salt settling systems to remove precipitated salt Sodium borohydride is often added to reduce corrosion of the equipment Evaporators for the membrane process are usually much simpler than those for the diaphragm process because the salt concentration in the membrane cell caustic solution is very low

3 3 2 4 Hydrogen Processing The hydrogen produced in all of the electrolytic processes contains small amounts of water vapor, sodium hydroxide, and salt which is removed through cooling The hydrogen produced during the mercury cell process also contains small amounts of mercury which must be removed by cooling the hydrogen gas to condense the mercury and treating with activated carbon

3 3 3 Raw Material Inputs and Pollution Outputs in the Production Line

Inputs and pollutant outputs of the chlor-alkali industry are relatively small both in number and volume in comparison to the chemical manufacturing industry as a whole The inputs are primarily salt and water as feedstocks, acids and chemical precipitants used to remove

impurities in the input brine or output chlorine and caustic soda, and freon used for liquefying and purifying the chlorine gas produced The major pollutant outputs from all three electrolytic processes are chlorine gas emissions (both fugitive and point source), spent acids, freon (both fugitive and point source), impurities removed from the input salt or brine, and pollutants originating from electrolytic cell materials and other system parts

Inputs and pollutant outputs from the auxiliary processes such as brine purification, chlorine processing, caustic soda processing, and hydrogen processing are described in Section 3 3 4

3 3 3 1 Mercury Cell Wastewater streams from mercury cell facilities arise from the chlorine drying process, brine purge, and miscellaneous sources Small amounts of mercury are found in the brine purge and miscellaneous sources which include floor sumps and cell wash water Before treatment, mercury concentrations (principally in the form of mercuric chloride, $HgCl_4^2$) typically range from 0 to 20 ppm Prior to treatment, sodium hydrosulfide is used to precipitate mercuric sulfide The mercuric sulfide is removed through filtration before the water is discharged

Air emissions consist of mercury vapor and chlorine gas released in relatively small amounts as fugitive emissions from the cells, and in the tail gases of the chlorine processing, caustic soda processing, and hydrogen processing Process tail gases are wet scrubbed with caustic soda or soda ash solutions to remove chlorine and mercury vapor Residual chlorine emissions in tail gases after treatment are less than one kilogram (kg) per 1,000 kg of chlorine produced and mercury emissions are negligible The tail gas scrubber water is typically reused as brine make-up water

Solid wastes containing mercury include solids generated during brine purification, spent graphite from decomposer cells, spent caustic filtration cartridges from the filtration of caustic soda solution, spilled mercury from facility sumps, and mercury cell "butters," which are semisolid amalgams of mercury with barium or iron formed when an excess of barium is used during salt purification

3 3 3 2 Diaphragm Cell Wastewater streams from the diaphragm cell process originate from the barometric condenser during caustic soda evaporation, chlorine drying, and from purification of salt recovered from the evaporators The use of lead and graphite anodes and asbestos diaphragms generates lead, asbestos, and chlorinated hydrocarbons in the caustic soda and chlorine processing waste streams Lead salts and chlorinated hydrocarbons are generated from corrosion of the anodes, and asbestos particles are formed by the degradation of the diaphragm with use Over the past twenty years, all but a few diaphragm cell facilities in the U S have switched from the use of lead and graphite anodes with asbestos diaphragms to DSA anodes and Modified Diaphragms which resist corrosion and degradation The lead, asbestos, and chlorinated hydrocarbon contaminants are, therefore, no longer discharged in significant amounts from most diaphragm cell chlor-alkali facilities Those facilities that discharged caustic processing wastewater streams to on-site lagoons may, however, still have significant levels of these contaminants on-site

Chlorine is released in relatively small amounts as fugitive emissions from the cells and in the process tail gases Process tail gases are wet scrubbed with soda ash or caustic soda solutions

to remove chlorine Residual chlorine emissions in tail gases after treatment are negligible The spent caustic solution is neutralized prior to discharge

Solid wastes generated in the diaphragm process consist primarily of solids generated during brine purification and scrapped cell parts including, cell covers, piping and used diaphragms Discarded cell parts are either land filled on-site, as is typically the case for spent diaphragms, or shipped off-site for disposal Used cathodes and DSA anodes are typically shipped off-site for recovery of their titanium content

3 3 3 3 Membrane Cell Wastewater from the membrane cell process originates from the barometric condenser during caustic soda evaporation, chlorine drying, and wash water from the ion exchange resin used to purify the brine solution The ion exchange wash water consists of dilute hydrochloric acid with small amounts of dissolved calcium, magnesium, and aluminum chloride The wastewater is combined with the other process wastewaters and treated by neutralization

Chlorine is released in relatively small amounts as fugitive emissions from the cells and in the process tail gases Process tail gases are wet scrubbed with soda ash or caustic soda solutions to remove chlorine Residual chlorine emissions in tail gases after treatment are negligible The spent caustic solution is neutralized prior to discharge

Solid waste generated in the diaphragm process consists primarily of solids generated during brine purification and used cell parts which include membranes, cathodes and DSA anodes The used membranes are typically returned to the supplier and the used cathodes and DSA anodes are shipped off-site for recovery of their titanium content

3 3 4 Auxiliary Processes

3 3 4 1 Brine Purification Brine solutions are typically treated with a number of chemicals to remove impurities prior to input to the electrolytic cells In the case of mercury and membrane cell systems, the brine is first acidified with HCl to remove dissolved chlorine Next, sodium hydroxide and sodium carbonate are added to precipitate calcium and magnesium ions as calcium carbonate and magnesium hydroxide Barium carbonate is then added to remove sulfates which precipitate out as barium sulfate The precipitants are removed from the brine solution by settling and filtration Pollutant outputs from this process include fugitive chlorine emissions and brine muds

Brine muds are one of the largest waste streams of the chlor-alkali industry On average, about 30 kg of brine mud are generated for every 1,000 kg of chlorine produced The volume of mud will vary, however, depending on the purity of the salt used Some facilities use pre-purified (i e , chemical grade) evaporated salts which will produce only 0 7 to 6 0 kg of brine mud per 1,000 kg of chlorine produced Brine mud typically contains magnesium hydroxide, calcium carbonate, and, in most cases, barium sulfate Mercury cell brine muds usually contain mercury either in the elemental form or as the complex ion, mercuric chloride ($HgCl_4^{2}$)

Brine muds are usually segregated from other process wastes and stored in lagoons on-site

When the lagoons become filled, the brine mud is either dredged and land filled off-site, or drained and covered over Some plants that use brine solution leached from subterranean deposits inject brine muds into the salt cavities that are no longer being used

3 3 4 2 Chlorine Processing The chlorine gas recovered from electrolytic cells is cooled to remove water vapor The condensed water is usually recycled as brine make-up although some facilities combine this waste stream with other waterborne waste streams prior to treatment The remaining water vapor is removed by scrubbing the chlorine gas with concentrated sulfuric acid The chlorine gas is then compressed and cooled to form liquid chlorine Between six kg and 35 kg of 79 percent sulfuric acid wastewater is generated per 1,000 kg of chlorine produced The majority of the spent sulfuric acid waste is shipped off-site for refortification to concentrated sulfuric acid or for use in other processes The remainder is used to control effluent pH and/or is discharged to water or land disposed

The process of purifying and liquefying impure chlorine gas involves the absorption of the chlorine in a stream of carbon tetrachloride The chlorine is subsequently removed in a stripping process in which the carbon tetrachloride is either recovered and reused, or is vented to the atmosphere

3 3 4 3 Caustic Soda Processing Caustic soda solution generated from chlor-alkali processes is typically processed to remove impurities and, in the case of the diaphragm and membrane processes, is concentrated to either a 50 percent or 73 percent water-based solution or to anhydrous caustic soda About five tons of water must be evaporated per ton of 50 percent caustic soda solution produced The water vapor from the evaporators is condensed in barometric condensers and, in the case of the diaphragm process, will primarily contain about 15 percent caustic soda solution and high concentrations of salt If sodium sulfate is not removed during the brine purification process, salt recovered from the evaporators is often recrystallized to avoid sulfate buildup in the brine If the salt is recrystallized, the wastewater from sodium hydroxide processing will also contain sodium sulfates Significant levels of copper may also be present in the wastewater due to corrosion of pipes and other equipment Wastewater from the membrane process contains caustic soda solution and virtually no salt or sodium sulfates

Caustic soda processing wastewater is typically neutralized with hydrochloric acid, lagooned, and then discharged directly to a receiving water or land disposed The caustic soda generated from the mercury process only requires filtration to remove mercury droplets which are typically recovered for reuse

3 3 4 4 Hydrogen Processing The hydrogen produced in all of the electrolytic processes contains small amounts of water vapor, sodium hydroxide, and salt which is removed through cooling Condensed salt water and sodium hydroxide solution is either recycled as brine make-up or treated with other waterborne waste streams The hydrogen produced during the mercury cell process, however, also contains small amounts of mercury which must be removed prior to liquefaction Most of the entrained mercury is extracted by cooling the gas The condensed mercury is then returned to the electrolytic cells Some facilities further purify the hydrogen gas of mercury using activated carbon treatment Spent activated carbon is typically shipped off-site as a hazardous waste

3 4 Summary of Health and Toxicity Effects of Selected Inorganic Chemicals

3 4 1 Hydrochloric Acid

Sources Hydrochloric acid is one of the highest volume chemicals produced by the inorganic chemical industry in the U S Some of its more common uses are as a pickling liquor and metal cleaner in the iron and steel industry, as an activator of petroleum wells, as a boiler scale remover, and as a neutralizer of caustic waste streams

Toxicity Hydrochloric acid is primarily a concern in its aerosol form Acid aerosols have been implicated in causing and exacerbating a variety of respiratory ailments Dermal exposure and ingestion of highly concentrated hydrochloric acid can result in corrosivity

Ecologically, accidental releases of solution forms of hydrochloric acid may adversely affect aquatic life by including a transient lowering of the pH (i e , increasing the acidity) of surface waters

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Releases of hydrochloric acid to surface waters and soils will be neutralized to an extent due to the buffering capacities of both systems The extent of these reactions will depend on the characteristics of the specific environment

Physical Properties Concentrated hydrochloric acid is highly corrosive

3 4 2 Chromium and Chromium Compounds

Sources Chrome pigments, chromates, chromic acid, chromium salts, and other inorganic chromium compounds are some of the larger volume products of the inorganic chemicals industry Chrome is used as a plating element for metal and plastics to prevent corrosion, and as a constituent of certain steels and inorganic pigments

Toxicity Although the naturally-occurring form of chromium metal has very low toxicity, chromium from industrial emissions is highly toxic due to strong oxidation characteristics and cell membrane permeability The majority of the effects detailed below are based on Chromium VI (an isomer that is more toxic than Cr III) Exposure to chromium metal and insoluble chromium salts affects the respiratory system Inhalation exposure to chromium and chromium salts may cause severe irritation of the upper respiratory tract and scarring of lung tissue Dermal exposure to chromium and chromium salts can also cause sensitive dermatitis and skin ulcers

Ecologically, although chromium is present in small quantities in all soils and plants, it is toxic to plants at higher soil concentrations (i e , 0 2 to 0 4 percent in soil)

Carcinogenicity Different sources disagree on the carcinogenicity of chromium Although an increased incidence in lung cancer among workers in the chromate-producing industry has been reported, data are inadequate to confirm that chromium is a human carcinogen Other

sources consider Chromium VI to be a known human carcinogen based on inhalation exposure

Environmental Fate Chromium is a non-volatile metal with very low solubility in water If applied to land, most chromium remains in the upper five centimeters of soil Most chromium in surface waters is present in particulate form as sediment Airborne chromium particles are relatively unreactive and are removed from the air through wet and dry deposition The precipitated chromium from the air enters surface water or soil Chromium bioaccumulates in plants and animals, with an observed bioaccumulation factor of 1,000,000 in snails

3 4 3 Carbonyl Sulfide

Sources Carbonyl sulfide is primarily generated by facilities that hydrolyze ammonium or potassium thiocyanate during the manufacturing of inorganic pigments and dyes

Toxicity Exposure to low to moderate concentrations of carbonyl sulfide causes eye and skin irritation and adverse central nervous system effects such as giddiness, headache, vertigo, amnesia, confusion, and unconsciousness If ingested, gastrointestinal effects include profuse salivation, nausea, vomiting and diarrhea Moderate carbonyl sulfide poisoning also causes rapid breathing and heartbeat, sweating, weakness, and muscle cramps Exposure to very high concentrations of carbonyl sulfide causes sudden collapse, unconsciousness, and death from sudden respiratory paralysis Recovery from sublethal exposure is slow, but generally complete Degradation products of carbonyl sulfide (especially hydrogen sulfide) can result in toxic symptoms and death

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate If released to soil or surface waters, carbonyl sulfide will rapidly volatilize It is not expected to adsorb to soil sediments or organic matter nor is it expected to bioconcentrate in fish and aquatic organisms Carbonyl sulfide is hydrolyzed in water to carbon dioxide and hydrogen sulfide Carbonyl sulfide is expected to have a long residence time in the atmosphere Atmospheric removal of carbonyl sulfide may occur by slow reactions with other gases, and may also occur through adsorption by plants and soil microbes

3 4 4 Manganese and Manganese Compounds

Sources Manganese is both a product and chemical intermediate of the inorganic chemical industry Manganese is used as a purifying and scavenging agent in metal production, as an intermediate in aluminum production and as a constituent of non-ferrous alloys to improve corrosion resistance and hardness

Toxicity There is currently no evidence that human exposure to manganese at levels commonly observed in ambient atmosphere results in adverse health effects

Chronic manganese poisoning bears some similarity to chronic lead poisoning Occurring via inhalation of manganese dust or fumes, it primarily involves the central nervous system Early symptoms include languor, speech disturbances, sleepiness, and cramping and weakness in

legs A stolid mask-like appearance of face, emotional disturbances such as absolute detachment broken by uncontrollable laughter, euphoria, and a spastic gait with a tendency to fall while walking are seen in more advanced cases Chronic manganese poisoning is reversible if treated early and exposure stopped Populations at greatest risk of manganese toxicity are the very young and those with iron deficiencies

Ecologically, although manganese is an essential nutrient for both plants and animals in excessive concentrations manganese inhibits plant growth

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Manganese is an essential nutrient for plants and animals As such, manganese accumulates in the top layers of soil or surface water sediments and cycles between the soil and living organisms It occurs mainly as a solid under environmental conditions, though may also be transported in the atmosphere as a vapor or dust

3 4 5 Ammonia

Sources Ammonia is used in many chemical manufacturing processes and is the building block for all synthetic nitrogen products Its prevalence and its volatile and water soluble characteristics allow it to be readily released to the air and water In the inorganic chemical manufacturing industry, ammonia can be either a feedstock or a by-product Some of the more common inorganic chemical industry processes using or producing ammonia include the manufacturing of ammonium chloride, ammonium hydroxide, ammonium thiosulfate, ammonium nitrate, hydrazine, and hydrogen cyanide

Toxicity Anhydrous ammonia is irritating to the skin, eyes, nose, throat, and upper respiratory system Ecologically, ammonia is a source of nitrogen (an essential element for aquatic plant growth), and may therefore contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters In addition, aqueous ammonia is moderately toxic to aquatic organisms

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Ammonia combines with sulfate ions in the atmosphere and is washed out by rainfall, resulting in rapid return of ammonia to the soil and surface waters Ammonia is a central compound in the environmental cycling of nitrogen Ammonia in lakes, rivers, and streams is converted to nitrate

Physical Properties Ammonia is a corrosive and severely irritating gas with a pungent odor

3 5 Pollution Prevention Opportunities

This section provides both general and company-specific descriptions of some pollution prevention advances that have been implemented within the inorganic chemical manufacturing industry While the list is not exhaustive, it does provide core information that can be used as the starting point for facilities interested in beginning their own pollution prevention projects

There have been numerous cases where the chemical industry has simultaneously reduced pollutant outputs and operating costs through pollution prevention techniques In the inorganic chemicals manufacturing sector, however, economically viable pollution prevention opportunities are not as easily identified as in other sectors The relatively small size and limited resources of a typical inorganic chemical facility limits the number of feasible pollution prevention options The limited resources available to the industry eliminates many pollution prevention options that require significant capital expenditures such as process modifications and process redesign In addition, the inorganic chemicals industry's products are primarily commodity chemicals for which the manufacturing processes have been developed over many years Commodity chemical manufacturers redesign their processes infrequently so that redesign of the reaction process or equipment is unlikely in the short term In addition, the industry's process equipment has been amortized over long periods of time making cost-effective process equipment improvements scarce As a result, pollution prevention in the inorganic chemicals industry is somewhat restricted to the less costly options, such as minor process modifications, operational changes, raw material substitutions, and recycling

3 5 1 Facility-Wide Opportunities

Pollution prevention in the inorganic chemical industry is process specific As such it is difficult to generalize about the relative merits of different pollution prevention strategies The age and size of the facility, and the type and number of its processes will determine the most effective pollution prevention strategy Brief descriptions of some of the more widespread, general pollution prevention techniques found to be effective at inorganic chemicals facilities are provided below It should be noted that many of the ideas identified below as pollution prevention opportunities, aimed at reducing wastes and reducing materials use, have been carried out by the chemicals manufacturing industry in the U S for many years as the primary means of improving process efficiencies and increasing profits

3 5 1 1 Use Membrane Cell Process In chlor-alkali production, pollution prevention options have been demonstrated for both the mercury cell and diaphragm cell processes, however, the best opportunity to reduce pollutant outputs, conserve energy, and reduce costs in the chlor-alkali industry are in the conversion to the membrane cell process In terms of energy consumption, the membrane cell process uses only about 77 percent of that of the mercury cell process and about 90 percent of that of the diaphragm cell process The membrane cell process also generates significantly less airborne and waterborne pollutants and solid wastes

3 5 1 2 Substitute Raw Materials The substitution or elimination of some of the raw materials used in the manufacturing of inorganic chemicals can result in substantial waste reductions and cost savings Because impurities in the feed stream can be a major contributor to waste generation, one of the most common substitutions is to use a higher purity feedstock This can be accomplished either by working with suppliers to get a higher quality feed or by installing purification equipment Raw materials can also be substituted with less toxic and less water soluble materials to reduce water contamination, and with less volatile materials to reduce fugitive emissions Sometimes certain raw materials can be eliminated all together The need for raw materials that end up as wastes should be reexamined to determine if raw materials can be eliminated by modifying the process and improving control

3 5 1 3 Improve Reactor Efficiencies Since the chemical products are primarily created inside the process reactor, it can be the primary source for waste (off-spec) materials One of the most important parameters dictating the reactor efficiency is the quality of mixing A number of techniques can be used to improve mixing, such as installing baffles in the reactor, a higher rotations per minute (rpm) motor for the agitator, a different mixing blade design, multiple impellers, and pump recirculation The method used to introduce feed to the reactor can also have an effect on the quality of mixing A feed distributor can be added to equalize residence time through the reactor, and feed streams can be added at a point in time closer to the ideal reactant concentration This will avoid secondary reactions which form unwanted by-products

3 5 1 4 Improve Catalyst The catalyst plays a critical role in the effectiveness of chemical conversion in the reactor Alternative chemical makeups and physical characteristics can lead to substantial improvements in the effectiveness and life of a catalyst Different catalysts can also eliminate by-product formation Noble metal catalysts can replace heavy metal catalysts to eliminate wastewater contaminated with heavy metals The consumption of catalysts can be reduced by using a more active form and emissions and effluents generated during catalyst activation can be eliminated by obtaining the catalyst in the active form

3 5 1 5 Optimize Processes Process changes that optimize reactions and raw materials use can reduce waste generation and releases Computer-controlled systems analyze the process continuously and respond more quickly and accurately than manual control systems These systems are often capable of automatic startups, shutdowns, and product changeover which can bring the process to stable conditions quickly, minimizing the generation of off-spec wastes Other process optimization techniques include equalizing the reactor and storage tank vent lines during batch filling to minimize vent gas losses, sequencing the addition of reactants and reagents to optimize yields and lower emissions, and optimizing sequences to minimize washing operations and cross-contamination of subsequent batches

3 5 1 6 Reduce Heat Exchanger Wastes and Inefficiencies Heat exchangers are often the source of significant off-spec product wastes generated by overheating the product closest to the tube walls The best way to reduce off-spec product from overheating is by reducing the heat exchanger tube wall temperature This can be accomplished through a number of techniques which do not reduce the overall heat transferred such as reducing the tube wall temperature and increasing the effective surface area of the heat exchanger, using staged heating by first heating with waste heat, then low pressure steam, followed by superheated high pressure steam, monitoring and preventing fouling of the heat exchanger tubes so that lower temperature heat sources can be used, and using noncorroding tubes which will foul less quickly than tubes that corrode

3 5 1 7 Improve Wastewater Treatment and Recycling A large portion of the inorganic chemical industry's pollutants leave the facilities as wastewater or wastewater treatment system sludge Improved treatment and minimization of wastewater are effective pollution prevention opportunities that often do not require significant changes to the industrial processes Modern wastewater treatment technologies such as ion exchange, electrolytic cells, reverse osmosis, and improved distillation, evaporation, and de-watering can often be added to existing treatment systems Wastewater streams containing acids or metals can be concentrated enough

to be sold commercially as a product by slightly altering the manufacturing process, adding processing steps, and segregating wastewater streams Furthermore, many wastewater streams can be reused within the same or different processes, significantly reducing discharges to the wastewater treatment system An ion exchange system installed in a mercury cell chlor-alkali plant reduced mercury by 99 percent in the facility's effluent An inorganic chemicals plant making photochemistry solution generated a wastewater containing silver Electrolytic cells were installed that recovered 98 percent of the silver and an evaporator was added that concentrated the remaining liquid for disposal resulting in a 90 percent reduction in waste volume

3 5 1 8 Prevent Leaks and Spills The elimination of sources of leaks and spills can be a very cost effective pollution prevention opportunity Leaks and spills can be prevented by installing seamless pumps and other "leakless" components, maintaining a preventative maintenance program, and maintaining a leak detection program

3 5 1 9 Improve Inventory Management and Storage Good inventory management can reduce the generation of wastes by preventing materials from exceeding their shelf life, preventing materials from being left over or not needed, and reducing the likelihood of accidental releases of stored material Designating a materials storage area, limiting traffic through the area, and giving one person the responsibility to maintain and distribute materials can reduce materials use, and the contamination and dispersal of materials

3 5 2 Opportunities from Process/Product Modifications

This section can be used as a diagnostic tool for identifying common pollution-creating problems that inorganic chemical processing facilities may experience Suggested solutions to prevent or reduce pollution loads, based on the latest data, follow each potential problem

3 5 2 1 By-products and Co-products

Quantity and Quality

Problem Process inefficiencies result in the generation of undesired by-products and co-products Inefficiencies will require larger volumes of raw materials and result in additional secondary products Inefficiencies can also increase fugitive emissions and wastes generated through material handling
Solution Increase product yield to reduce by-product and co-product generation and raw material requirements

Uses and Outlets

Problem By-products and co-products are not fully utilized, generating material or waste that must be managed
Solution Identify uses and develop a sales outlet Collect information necessary to firm up a purchase commitment such as minimum quality criteria, maximum impurity levels that can be tolerated, and performance criteria

3 5 2 2 Catalysts

Composition

Problem The presence of heavy metals in catalysts can result in contaminated process wastewater from catalyst handling and separation These wastes may require special treatment and disposal procedures or facilities Heavy metals can be inhibitory or toxic to biological wastewater treatment units Sludge from wastewater treatment units may be classified as hazardous due to heavy metals content Heavy metals generally exhibit low toxicity thresholds in aquatic environments and may bioaccumulate
Solution Catalysts comprised of noble metals, because of their cost, can be recycled by both on-site and off-site reclaimers

Preparation and Handling

Problem Emissions or effluents are generated with catalyst activation or regeneration
Solution Obtain catalyst in the active form Provide in situ activation with appropriate processing/activation facilities

Problem Catalyst attrition and carry over into product requires de-ashing facilities which are a likely source of wastewater and solid waste
Solution Develop a more robust catalyst or support

Problem Catalyst is spent and needs to be replaced
Solution In situ regeneration eliminates unloading/loading emissions and effluents versus off-site regeneration or disposal

Problem Pyrophoric catalyst needs to be kept wet, resulting in liquid contaminated with metals
Solution Use a non-pyrophoric catalyst Minimize amount of water required to handle and store safely

Problem Short catalyst life
Solution Study and identify catalyst deactivation mechanisms Avoid conditions which promote thermal or chemical deactivation By extending catalyst life, emissions and effluents associated with catalyst handling and regeneration can be reduced

Effectiveness

Problem Catalyzed reaction has by-product formation, incomplete conversion and less-than-perfect yield
Solution Reduce catalyst consumption with a more active form A higher concentration of active ingredient or increased surface area can reduce catalyst loadings Use a more selective catalyst which will reduce the yield of undesired by-products Improve reactor mixing/contacting to increase catalyst effectiveness Develop a thorough understanding of reaction to allow optimization of reactor design Include in the optimization, catalyst consumption and by-product yield

3 5 2 3 Intermediate Products

Quantity and Quality

Problem Intermediate reaction products or chemical species, including trace levels of toxic constituents, may contribute to process waste under both normal and upset conditions
Solution Modify reaction sequence to reduce amount or change composition of intermediates

Problem Intermediates may contain toxic constituents or have characteristics that are harmful to the environment
Solution Modify reaction sequence to change intermediate properties Use equipment design and process control to reduce releases

3 5 2 4 Process Conditions/Configuration

Temperature

Problem High heat exchange tube temperatures cause thermal cracking/decomposition of many by-products These lower molecular weight by-products are a source of "light ends" and fugitive emissions High localized temperature gives rise to polymerization of reactive monomers, resulting in "heavies" or "tars " Such materials can foul heat exchange equipment or plug fixed-bed reactors, thereby requiring costly equipment cleaning and production outage
Solution Select operating temperatures at or near ambient temperature whenever possible Use lower pressure steam to lower temperatures Use intermediate exchangers to avoid contact with furnace tubes and walls Use staged heating to minimize product degradation and unwanted side reactions Use a super heat of high-pressure steam in place of furnace Monitor exchanger fouling to correlate process conditions which increase fouling, avoid conditions which rapidly foul exchangers Use on-line tube cleaning technologies to keep tube surfaces clean to increase heat transfer Use scraped wall exchangers in viscous service Use falling film reboiler, pumped recirculation reboiler or high-flux tubes

Problem Higher operating temperatures imply "heat input" usually via combustion which generates emissions
Solution Explore heat integration opportunities (e g , use waste heat to preheat materials and reduce the amount of combustion required)

Problem Heat sources such as furnaces and boilers are a source of combustion emissions
Solution Use thermocompressor to upgrade low-pressure steam to avoid the need for additional boilers and furnaces

Problem Vapor pressure increases with increasing temperature Loading/unloading, tankage and fugitive emissions generally increase with increasing vapor pressure
Solution If possible, cool materials before sending to storage Use hot process streams to reheat feeds Add vent condensers to recover vapors in storage tanks or process Add closed dome loading with vapor recovery condensers

Problem Water solubility of most chemicals increases with increasing temperature
Solution Use lower temperature (vacuum processing)

Pressure

Problem Fugitive emissions from equipment
Solution Equipment operating in vacuum service is not a source of fugitives, however, leaks into the process require control when system is degassed

Problem Seal leakage potential due to pressure differential
Solution Minimize operating pressure

Problem Gas solubility increases with higher pressures
Solution Determine whether gases can be recovered, compressed, and reused or require controls

Corrosive Environment

Problem Material contamination occurs from corrosion products Equipment failures result in spills, leaks, and increased maintenance costs
Solution Neutralize corrosivity of materials contacting equipment Use corrosion inhibitors Improve metallurgy or provide coating or lining Improve metallurgy or provide coating or lining or operate in a less corrosive environment

Problem Increased waste generation due to addition of corrosion inhibitors or neutralization
Solution Improve metallurgy or provide coating or lining Improve metallurgy or provide coating or lining or operate in a less corrosive environment

Batch vs Continuous Operations

Problem Vent gas lost during batch fill
Solution Equalize reactor and storage tank vent lines Recover vapors through condenser, adsorber, etc

Problem Waste generated by cleaning/purging of process equipment between production batches
Solution Use materials with low viscosity Minimize equipment roughness Optimize product manufacturing sequence to minimize washing operations and cross-contamination of subsequent batches

Problem Process inefficiencies lower yield and increase emissions
Solution Sequence addition of reactants and reagents to optimize yields and lower emissions

Problem Continuous process fugitive emissions and waste increase over time due to equipment failure through a lack of maintenance between turnarounds
Solution Design facility to readily allow maintenance so as to avoid unexpected equipment failure and resultant release

Process Operation/Design

Problem Numerous processing steps create wastes and opportunities for errors
Solution Keep it simple Make sure all operations are necessary More operations and complexity only tend to increase potential emission and waste sources

Problem Non-reactant materials (solvents, absorbents, etc) create wastes Each chemical

(including water) employed within the process introduces additional potential waste sources the composition generated wastes also tends to become more complex
Solution Evaluate unit operation or technologies (e g , separation) that do not require the addition of solvents or other non-reactant chemicals

Problem High conversion with low yield results in wastes
Solution Recycle operations generally improve overall use of raw materials and chemicals, thereby increasing the yield of desired products while at the same time reducing the generation of wastes A case-in-point is to operate at a lower conversion per reaction cycle by reducing catalyst consumption, temperature, or residence time Many times, this can result in a higher selectivity to desired products The net effect upon recycle of unreacted reagents is an increase in product yield, while at the same time reducing the quantities of spent catalyst and less desirable by-products

Problem Non-regenerative treatment systems result in increased waste versus regenerative systems
Solution Regenerative fixed bed treating or desiccant operation (e g , aluminum oxide, silica, activated carbon, molecular sieves, etc) will generate less quantities of solid or liquid waste than non-regenerative units (e g , calcium chloride or activated clay) With regenerative units though, emissions during bed activation and regeneration can be significant Further, side reactions during activation/regeneration can give rise to problematic pollutants

3 5 2 5 Product

Process Chemistry

Problem Insufficient R&D into alternative reaction pathways may miss pollution opportunities such as reducing waste or eliminating a hazardous constituent
Solution R&D during process conception and laboratory studies should thoroughly investigate alternatives in process chemistry that affect pollution prevention

Product Formulation

Problem Product based on end-use performance may have undesirable environmental impacts or use raw materials or components that generate excessive or hazardous wastes
Solution Reformulate products by substituting different material or using a mixture of individual chemicals that meet end-use performance specifications

3 5 2 6 Raw Materials

Purity

Problem Impurities may produce unwanted by-products and waste Toxic impurities, even in trace amounts, can make a waste hazardous and therefore subject to strict and costly regulation
Solution Use higher purity materials Purify materials before use and reuse if practical Use inhibitors to prevent side reactions

Problem Excessive impurities may require more processing and equipment to meet product specifications, increasing costs and potential for fugitive emissions, leaks, and spills
Solution Achieve balance between feed purity, processing steps, product quality, and waste generation

Problem Specifying a purity greater than needed by the process increases costs and can generate more waste generation by the supplier
Solution Specify a purity no greater than what the process needs

Problem Impurities in clean air can increase inert purges
Solution Use pure oxygen

Problem Impurities may poison catalyst prematurely resulting in increased wastes due to yield loss and more frequent catalyst replacement
Solution Install guard beds to protect catalysts

Vapor Pressure

Problem Higher vapor pressures increase fugitive emissions in material handling and storage
Solution Use materials with lower vapor pressure and higher odor threshold

Problem High vapor pressure with low odor threshold materials can cause nuisance odors
Solution Use material with lower vapor pressure

Water Solubility

Problem Toxic or non-biodegradable materials that are water soluble may affect wastewater treatment operation, efficiency, and cost
Solution Use less toxic or more biodegradable materials

Problem Higher solubility may increase potential for surface and groundwater contamination and may require more careful spill prevention, containment, and cleanup plans
Solution Use less soluble materials

Problem Higher solubility may increase potential for storm water contamination in open areas
Solution Use less soluble materials Prevent direct contact with storm water by diking or covering areas

Problem Process wastewater associated with water washing or hydrocarbon/water phase separation will be impacted by containment solubility in water Appropriate wastewater treatment will be impacted
Solution Use less toxic or more biodegradable materials Minimize water usage Reuse wash water Determine optimum process conditions for phase separation Evaluate alternative separation technologies (coalescers, membranes, distillation, etc)

Toxicity

Problem Community and worker safety and health concerns result from routine and non-routine emissions Emissions sources include vents, equipment leaks, wastewater emissions, emergency pressure relief, etc
Solution Use less toxic materials Reduce exposure through equipment design and process control Use systems which are passive for emergency containment of toxic releases

Problem Surges or higher than normal continuous levels of toxic materials can shock or miss wastewater biological treatment systems resulting in possible fines and possible toxicity in the

receiving water
Solution Use less toxic material Reduce spills, leaks, and upset conditions through equipment and process control Consider effect of chemicals on biological treatment, provide unit pretreatment or diversion capacity to remove toxicity Install surge capacity for flow and concentration equalization

Form of Supply

Problem Small containers increase shipping frequency which increases chances of material releases and waste residues from shipping containers (including wash waters)
Solution Use bulk supply, ship by pipeline, or use "jumbo" drums or sacks In some cases, product may be shipped out in the same containers the material supply was shipped in without washing

Problem Nonreturnable containers may increase waste
Solution Use returnable shipping containers or drums

Handling and Storage

Problem Physical state (solid, liquid, gaseous) may raise unique environmental, safety, and health issues with unloading operations and transfer to process equipment
Solution Use equipment and controls appropriate to the type of materials to control releases

Problem Large inventories can lead to spills, inherent safety issues and material expiration
Solution Minimize inventory by utilizing just-in-time delivery

3 5 2 7 Waste Streams

Quantity and Quality

Problem Characteristics and sources of waste streams are unknown
Solution Document sources and quantities of waste streams prior to pollution prevention assessment

Problem Wastes are generated as part of the process
Solution Determine what changes in process conditions would lower waste generation of toxicity Determine if wastes can be recycled back into the process

Composition

Problem Hazardous or toxic constituents are found in waste streams Examples are sulfides, heavy metals, halogenated hydrocarbons, and polynuclear aromatics
Solution Evaluate whether different process conditions, routes, or reagent chemicals (e g , solvent catalysts) can be substituted or changed to reduce or eliminate hazardous or toxic compounds

Properties

Problem Environmental fate and waste properties are not known or understood
Solution Evaluate waste characteristics using the following type properties corrosivity, ignitability, reactivity, BTU content (energy recovery), biodegradability, aquatic toxicity, and bioaccumulation potential of the waste and of its degradable products, and whether it is a

solid, liquid, or gas

Disposal

Problem Ability to treat and manage hazardous and toxic waste unknown or limited
Solution Consider and evaluate all on-site and off-site recycle, reuse, treatment, and disposal options available Determine availability of facilities to treat or manage wastes generated

Exhibit 3-2 Pollution Preventing Equipment Modifications

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Compressors blowers fans	▪ Shaft seal leaks piston rod seal leaks and vent streams	▪ Seal less designs (diaphragmatic hermetic or magnetics) ▪ Design for low emissions (internal balancing double inlet gland eductors) ▪ Shaft seal designs (carbon rings double mechanical seals buffered seals) ▪ Double seal with barrier fluid vented to control device	▪ Preventive maintenance program
Concrete pads floors sumps	▪ Leaks to groundwater	▪ Water stops ▪ Embedded metal plates ▪ Epoxy sealing ▪ Other impervious sealing	▪ Reduce unnecessary purges transfers and sampling ▪ Use drip pans where necessary

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Controls	▪ Shutdowns and start-ups generate waste and releases	▪ Improve on-line controls ▪ On-line instrumentation ▪ Automatic start-up and shutdown ▪ On line vibration analysis ▪ Use consensus systems (e g shutdown trip requires two out of three affirmative responses)	▪ Continuous versus batch ▪ Optimize on line run time ▪ Optimize shutdown interlock inspection frequency ▪ Identify safety and environment critical instruments and equipment
Distillation	▪ Impurities remain in process streams ▪ Large amounts of contaminated water condensate from stream stripping	▪ Increase reflux ratio ▪ Add section to column ▪ Column intervals ▪ Change feed tray ▪ Insulate to prevent heat loss ▪ Preheat column feed ▪ Increase vapor line size to lower pressure drop ▪ Use reboilers or inert gas stripping agents	▪ Change column operating conditions - reflux ratio - feed tray - temperature pressure etc ▪ Clean column to reduce fouling ▪ Use higher temperature steam

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
General manufacturing equipment areas	▪ Contaminated rainwater	▪ Provide roof over process facilities	▪ Return samples to process
		▪ Segregate process discharge system from storm drainage system (diking)	▪ Monitor storm water discharge
		▪ Hard-pipe process streams to process discharge system	
	▪ Contaminated sprinkler and fire water	▪ Seal floors	
		▪ Drain to sump	
		▪ Route to waste treatment	
	▪ Leaks and emissions during cleaning	▪ Design for cleaning	▪ Use drip pans for maintenance activities
		▪ Design for minimum rinsing	▪ Rinse to sump
		▪ Design for minimum sludge	▪ Reuse cleaning solutions
		▪ Provide vapor enclosure	
		▪ Drain to process	

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Heat exchangers	▪ Increased waste due to high localized temperatures	▪ Use intermediate exchangers to avoid contact with furnace tubes and walls ▪ Use staged heating to minimize product degradation and unwanted side reactions (waste heat > > low pressure steam > > high pressure steam) ▪ Use scraped wall exchangers in viscous service ▪ Using falling film reboiler piped recirculation reboiler or high-flux tubes ▪ Use lowest pressure steam possible	▪ Select operating temperatures at or near ambient temperature when ever possible These are generally most desirable from a pollution prevention standpoint ▪ Use lower pressure steam to lower temperatures ▪ Monitor exchanger fouling to correlate process conditions which increase fouling avoid conditions which rapidly foul exchangers ▪ Use on-line tube cleaning techniques to keep tube surfaces clean
	▪ Contaminated materials due to tubes leaking at tube sheets ▪ Furnace emissions	▪ Use welded tubes or double tube sheets with inert purge Mount vertically ▪ Use super heat of high pressure steam in place of a furnace	▪ Monitor for leaks

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Piping	▪ Leaks to groundwater/ fugitive emissions	▪ Design equipment layout so as to minimize pipe run length ▪ Eliminate underground piping or design for cathodic protection if necessary to install piping underground ▪ Use welded fittings ▪ Reduce number of flanges and valves ▪ Use all welded pipe ▪ Use secondary containment ▪ Use spiral wound gaskets ▪ Use plugs and double valves for open end lines ▪ Change metallurgy ▪ Use lined pipe	▪ Monitor for corrosion and erosion ▪ Paint to prevent external corrosion
	▪ Releases when cleaning or purging lines	▪ Use pigs for cleaning ▪ Slope to low point drain ▪ Use heat tracing and insulation to prevent freezing ▪ Install equalizer lines	▪ Flush to product storage tank

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Pumps	▪ Fugitive emissions from shaft seal leaks	▪ Mechanical seal in lieu of packing	▪ Seal installation practices
		▪ Double mechanical seal with inert barrier fluid	▪ Monitor for leaks
		▪ Double machined seal with barrier fluid vented to control device	
		▪ Seal less pump (canned motor magnetic drive)	
		▪ Vertical pump	
	▪ Fugitive emissions from shaft seal leaks	▪ Use pressure transfer to eliminate pump	
	▪ Residual heel of liquid during pump maintenance	▪ Low point drain on pump casing	▪ Flush casing to process discharge system for treatment
			▪ Increase the mean time between pump failures by selecting proper seal material aligning well reducing pipe induced stress maintaining seal lubrication
	▪ Injection of seal flush fluid into process stream	▪ Use double mechanical seal with inert barrier fluid where practical	

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Reactors	▪ Poor conversion or performance due to inadequate mixing	▪ Static mixing ▪ Add baffles ▪ Change impellers ▪ Add horsepower ▪ Add distributor	▪ Add ingredients with optimum sequence ▪ Allow proper head space in reactor to enhance vortex effect
	▪ Waste by product formation	▪ Provide separate reactor for converting recycle streams to usable products	▪ Optimize reaction conditions (temperature pressure etc)
Relief Valve	▪ Leaks	▪ Provide upstream rupture disc	
	▪ Fugitive emissions	▪ Vent to control or recovery device	▪ Monitor for leaks and for control efficiency
	▪ Discharge to environment from over pressure	▪ Pump discharges to suction of pump ▪ Thermal relief to tanks ▪ Avoid discharge to roof areas to prevent contamination of rainwater	▪ Monitor for leaks
	▪ Frequent relief	▪ Use pilot operated relief valve ▪ Increase margin between design and operating pressure	▪ Reduce operating pressure ▪ Review system performance

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Sampling	▪ Waste generation due to sampling (disposal containers leaks fugitives etc)	▪ In line in situ analyzers ▪ System for return to process ▪ Closed loop ▪ Drain to sump	▪ Reduce number and size of samples required ▪ Sample at the lowest possible temperature ▪ Cool before sampling
Tanks	▪ Tank breathing and working losses	▪ Cool materials before storage ▪ Insulate tanks ▪ Vent to control device (flare condenser etc) ▪ Vapor balancing ▪ Floating roof ▪ Higher design pressure	▪ Optimize storage conditions to reduce losses
	▪ Leak to groundwater	▪ All aboveground (situated so bottom can routinely be checked for leads) ▪ Secondary containment ▪ Improve corrosion resistance	▪ Monitor for leaks and corrosion
	▪ Large waste heel	▪ Design for 100 % de inventory	▪ Recycle to process if practical
Vacuum Systems	▪ Waste discharge from jets	▪ Substitute mechanical vacuum pump ▪ Evaluate using process fluid for powering jet	▪ Monitor for air leaks ▪ Recycle condensate to process

Equipment	Potential Environment Problem	Possible Approach	
		Design Related	Operational Related
Valves	▪ Fugitive emissions from leaks	▪ Bellow seals ▪ Reduce number where practical ▪ Special packing sets	▪ Stringent adherence to packing procedures
Vents	▪ Release to environment	▪ Route to control or recovery device	▪ Monitor performance

CHAPTER 4
PETROLEUM REFINING[3]

4 1 Introduction

Petroleum refining is the physical, thermal and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products For the purposes of this manual petroleum refining includes petroleum products produced through the distillation and fractionation of crude oil, re-distillation of unfinished petroleum derivatives cracking, or other processes

4 2 Product Characterization

The primary products of the industry fall into three major categories fuels (motor gasoline diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil kerosene and coke), finished non-fuel products (solvents, lubricating oils, greases, petroleum wax, petroleum jelly asphalt, and coke), and chemical industry feedstocks (naphtha, ethane propane butane ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene) These petroleum products are used for energy and as primary input to a vast number of products including fertilizers, pesticides, paints, waxes thinners, solvents, cleaning fluids, detergents refrigerants anti-freeze, resins, sealants, insulations, latex, rubber compounds, hard plastics plastic sheeting, plastic foam and synthetic fibers

4 3 Industrial Process Description

This section describes the major industrial processes within the petroleum refining industry including the materials and equipment used, and the processes employed This discussion also provides a concise description of where wastes may be produced in the process and describes the potential fate (via air, water, and soil pathways) of these waste products

4 3 1 Industrial Processes in the Petroleum Refining Industry

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities The composition of crude oil can vary significantly depending on its source Petroleum refineries are a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products For these reasons, no two refineries are alike Portions of the outputs from some processes are re-fed back into the same process, fed to new processes, fed back to a previous process, or blended with other outputs to

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[3] The information in this chapter is derived from the U S Environmental Protection Agency's Office of Compliance Sector Notebook Project, *Profile of the Petroleum Refining Industry*, September 1995 (document # EPA/310-R-95-013) Readers should refer to that document for a comprehensive set of references and sources Contact your local EP3 Clearinghouse for a copy of the EPA document or for information on how to access it electronically via the Internet

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form finished products The major unit operations typically involved at petroleum refineries are described briefly below

Refining crude oil into useful petroleum products can be separated into two phases and a number of supporting operations The first phase is desalting of crude oil and the subsequent distillation into its various components or "fractions " The second phase is made up of three different types of "downstream" processes combining, breaking, and reshaping Downstream processes convert some of the distillation fractions into petroleum products (residual fuel oil gasoline kerosene, etc) through any combination of different cracking, coking, reforming, and alkylation processes Supporting operations may include wastewater treatment, sulfur recovery additive production, heat exchanger cleaning, blowdown systems, blending of products, and storage of products

4 3 1 1 Crude Oil Distillation and Desalting One of the most important operations in a refinery is the initial distillation of the crude oil into its various boiling point fractions Distillation involves the heating, vaporization, fractionation, condensation, and cooling of feedstocks This section discusses the atmospheric and vacuum distillation processes which when used in sequence result in lower costs and higher efficiencies This section also discusses the important first step of desalting the crude oil prior to distillation

4 3 1 1 1 Desalting Before separation into fractions, crude oil usually must first be treated to remove corrosive salts The desalting process also removes some of the metals and suspended solids which cause catalyst deactivation Desalting involves the mixing of heated crude oil with water (about three to 10 percent of the crude oil volume) so that the salts are dissolved in the water The water must then be separated from the crude oil in a separating vessel by adding demulsifier chemicals to assist in breaking the emulsion and/or, more commonly, by applying a high potential electric field across the settling vessel to coalesce the polar salt water droplets The desalting process creates an oily desalter sludge and a high temperature salt water waste stream which is typically added to other process wastewaters for treatment in the refinery wastewater treatment facilities The water used in crude desalting is often untreated or partially treated water from other refining process water sources

4 3 1 1 2 Atmospheric Distillation The desalted crude oil is then heated in a heat exchanger and furnace to about 398°C and fed to a vertical, distillation column at atmospheric pressure where most of the feed is vaporized and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature The lighter fractions condense and are collected towards the top of the column Heavier fractions, which may not vaporize in the column, are further separated later by vacuum distillation Within each atmospheric distillation tower, a number of side streams (at least four) of low-boiling point components are removed from the tower from different trays These low-boiling point mixtures are in equilibrium with heavier components which must be removed The side streams are each sent to a different small stripping tower containing four to 10 trays with steam injected under the bottom tray The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side stream draw tray Fractions obtained from atmospheric distillation include naphtha, gasoline, kerosene, light fuel oil, diesel oils, gas oil, lube distillate, and heavy bottoms Most of these can be sold as finished products, or blended with products from downstream

processes Another product produced in atmospheric distillation as well as many other refinery processes, is the light, non-condensable refinery fuel gas (mainly methane and ethane) Typically this gas also contains hydrogen sulfide and ammonia gases The mixture of these gases is known as "sour gas" or "acid gas " The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces Air emissions during atmospheric distillation arise from the combustion of fuels in the furnaces to heat the crude oil, process vents and fugitive emissions Oily sour water (condensed steam containing hydrogen sulfate and ammonia) and oil is also generated in the fractionators

4 3 1 1 3 Vacuum Distillation Heavier fractions from the atmospheric distillation unit that cannot be distilled without cracking under its pressure and temperature conditions are vacuum distilled Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure to increase volatilization and separation In most systems, the vacuum inside the fractionator is maintained with steam ejectors and vacuum pumps, barometric condensers or surface condensers The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporization and separation The heavier fractions from the vacuum distillation column are processed downstream into more valuable products through either cracking or coking operations

A potential source of emissions from distillation of crude oil are the combustion of fuels in the furnace and some light gases leaving the top of the condensers on the vacuum distillation column A certain amount of non-condensable light hydrocarbons and hydrogen sulfide pass through the condenser to a hot well, and then are discharged to the refinery sour fuel system or are vented to a process heater, flare or another control device to destroy hydrogen sulfide The quantity of these emissions depends on the size of the unit, the type of feedstock, and the cooling water temperature If barometric condensers are used in vacuum distillation, significant amounts of oily wastewater can be generated Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily wastewater stream Oily sour water is also generated in the fractionators

4 3 1 2 Downstream Processing Certain fractions from the distillation of crude oil are further refined in thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, hydrotreating, alkylation, isomerization, polymerization, catalytic reforming, solvent extraction, merox, de-waxing, propane de-asphalting and other operations These downstream processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules For many of the operations discussed below, a number of different techniques are used in the industry While the major techniques used for each process are described, it is not possible to discuss all of the different processes currently in use

4 3 1 2 1 Thermal Cracking/Visbreaking Thermal cracking, or visbreaking, uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules The process has been largely replaced by catalytic cracking and some refineries no longer employ thermal cracking Both processes reduce the production of less valuable products such as heavy fuel oil and cutter stock and increase the feed stock to the catalytic cracker and gasoline yields In thermal cracking, heavy gas oils and residue from the vacuum distillation process are typically the feed stocks The feed stock is heated in a furnace or other thermal unit to up to 537°C and

then fed to a pressurized reaction chamber Following the reactor step, the process stream is mixed with a cooler recycle stream which stops the cracking reactions The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporize and are drawn off The lighter products are fed to a fractionating tower where the various fractions are separated The "bottoms" consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber, the remaining bottoms are usually blended into residual fuel

Air emissions from thermal cracking include emissions from the combustion of fuels in the process heater, vents, and fugitive emissions A sour water stream is generated in the fractionator

4 3 1 2 2 Coking Coking is a cracking process used primarily to reduce refinery production of low-value residual fuel oils to transportation fuels, such as gasoline and diesel As part of the upgrading process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities, and is used as a fuel for power plants if the sulfur content is low enough Coke also has non-fuel applications as a raw material for many carbon and graphite products including anodes for the production of aluminum, and furnace electrodes for the production of elemental phosphorus, titanium dioxide, calcium carbide and silicon carbide A number of different processes are used to produce coke, "delayed coking" is the most widely used today, but "fluid coking" is expected to be an important process in the future Fluid coking produces a higher grade of coke which is increasingly in demand In delayed coking operations the same basic process as thermal cracking is used except feed streams are allowed to react longer without being cooled The delayed coking feed stream of residual oils from various upstream processes is first introduced to a fractionating tower where residual lighter materials are drawn off and the heavy ends are condensed The heavy ends are removed and heated in a furnace to about 481°- 537°C and then fed to an insulated vessel called a coke drum where the coke is formed When the coke drum is filled with product, the feed is switched to an empty parallel drum Hot vapors from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulfide, and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products Steam is then injected into the full coke drum to remove hydrocarbon vapors, water is injected to cool the coke and the coke is removed Typically, high pressure water jets are used to cut the coke from the drum

Air emissions from coking operations include the process heater flue gas emissions, fugitive emissions and emissions that may arise from the removal of the coke from the coke drum The injected steam is condensed and the remaining vapors are typically flared Wastewater is generated from the coke removal and cooling operations and from the steam injection In addition, the removal of coke from the drum can release particulate emissions and any remaining hydrocarbons to the atmosphere

4 3 1 2 3 Catalytic Cracking Catalytic cracking uses heat, pressure and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules Catalytic cracking has largely replaced thermal cracking because it is able to produce more gasoline with a higher octane and less heavy fuel oils and light gases Feed stocks are light and heavy oils from the crude oil distillation unit which are processed primarily into gasoline as well as some fuel oil and light gases Most catalysts used in catalytic cracking consist of mixtures of crystalline synthetic silica-

alumina termed "zeolites,' and amorphous svnthetic silica-alumina The catalytic cracking processes, as well as most other refinery catalvtic processes produce coke which collects on the catalyst surface and diminishes its catalytic properties The catalyst, therefore, needs to be regenerated continuously or periodically essentially by burning the coke off the catalvst at high temperatures The method and frequency in which catalysts are regenerated are a major factor in the design of catalytic cracking units A number of different catalytic cracking designs are currently in use in the U S , including fixed-bed reactors, moving-bed reactors, fluidized-bed reactors, and once-through units The fluidized- and moving-bed reactors are bv far the most prevalent

Fluidized-bed catalytic cracking units (FCCUs) are by far the most common catalytic cracking units In the fluidized-bed process, oil and oil vapor pre-heated to 260 to 426°C is contacted with hot catalyst at about 703°C either in the reactor itself or in the feed line (riser) to the reactor The catalyst is in a fine, granular form which, when mixed with the vapor, has many of the properties of a fluid The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in the reactor and any oil remaining on the catalyst is removed by steam stripping The cracked oil vapors are then fed to a fractionation tower where the various desired fractions are separated and collected The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration by burning off the coke deposits with air

In the moving-bed process, oil is heated to up to 703°C and is passed under pressure through the reactor where it comes into contact with a catalyst flow in the form of beads or pellets The cracked products then flow to a fractionating tower where the various compounds are separated and collected The catalyst is regenerated in a continuous process where deposits of coke on the catalyst are burned off Some units also use steam to strip remaining hydrocarbons and oxygen from the catalyst before being fed back to the oil stream In recent years moving-bed reactors have largely been replaced by fluidized-bed reactors

Catalytic cracking is one of the most significant sources of air pollutants at refineries Air emissions from catalytic cracking operations include the process heater flue gas emissions, fugitive emissions, and emissions generated during regeneration of the catalyst Relatively high concentrations of carbon monoxide can be produced during regeneration of the catalyst which is typically converted to carbon dioxide either in the regenerator or further downstream in a carbon monoxide waste heat boiler In addition, a significant amount of fine catalyst dust is produced in FCCUs as a result of the constant movement of the catalyst grains against each other Much of this dust, consisting primarily of alumina and relatively small amounts of nickel, is carried with the carbon monoxide stream to the carbon monoxide burner The catalyst dust is then separated from the resulting carbon dioxide stream via cyclones and/or electrostatic precipitators and is sent off-site for disposal or treatment Generated wastewater is typically sour water from the fractionator containing some oil and phenols Wastewater containing metal impurities from the feed oil can also be generated from the steam used to purge and regenerate catalysts

4 3 1 2 4 Catalytic Hydrocracking Catalytic hydrocracking normally utilizes a fixed-bed catalytic cracking reactor with cracking occurring under substantial pressure in the presence of hydrogen Feedstocks to hydrocracking units are often those fractions that are the most difficult to crack and cannot be cracked effectively in catalytic cracking units These include middle distillates, cycle oils, residual fuel oils and reduced crudes The hydrogen suppresses the

formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products However, this process also breaks the heavy, sulfur and nitrogen bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst For this reason, the feedstock is often first hydrotreated to remove impurities before being sent to the catalytic hydrocracker Sometimes hydrotreating is accomplished by using the first reactor of the hydrocracking process to remove impurities Water also has a detrimental effect on some hydrocracking catalysts and must be removed before being fed to the reactor The water is removed by passing the feed stream through a silica gel or molecular sieve drver Depending on the products desired and the size of the unit, catalytic hydrocracking is conducted in either single stage or multi-stage reactor processes Most catalysts consist of a crystalline mixture of silica-alumina with small amounts of rare earth metals

Hydrocracking feedstocks are usually first hydrotreated to remove the hydrogen sulfide and ammonia that will poison the catalyst Sour gas and sour water streams are produced at the fractionator, however, if the hydrocracking feedstocks are first hydrotreated to remove impurities, both streams will contain relatively low levels of hydrogen sulfide and ammonia Hydrocracking catalysts are typically regenerated off-site after two to four years of operation Therefore, little or no emissions are generated from the regeneration processes Air emissions arise from the process heater, vents, and fugitive emissions

4 3 1 2 5 Hydrotreating/Hydroprocessing Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulfur, nitrogen, oxygen halides and trace metal impurities that may deactivate process catalysts Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels Hydroprocessing, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter, more saleable products Both hydrotreating and hydroprocessing units are usually placed upstream of those processes in which sulfur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units The processes utilize catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen The reactors are nearly all fixed-bed with catalyst replacement or regeneration done after months or years of operation often at an off-site facility In addition to the treated products the process produces a stream of light fuel gases hydrogen sulfide and ammonia The treated product and hydrogen-rich gas are cooled after they leave the reactor before being separated The hydrogen is recycled to the reactor

The off-gas stream may be very rich in hydrogen sulfide and light fuel gas The fuel gas and hydrogen sulfide are typically sent to the sour gas treatment unit and sulfur recovery unit Catalysts are typically cobalt or molybdenum oxides on alumina, but can also contain nickel and tungsten Air emissions from hydrotreating may arise from process heater flue gas, vents, and fugitive emissions

4 3 1 2 6 Alkylation Alkylation is used to produce a high octane gasoline blending stock from the isobutane formed primarily during catalytic cracking and coking operations, but also from catalytic reforming, crude distillation and natural gas processing Alkylation joins an olefin and an isoparaffin compound using either a sulfuric acid or hydrofluoric acid catalyst The products are alkylates including propane and butane liquids When the concentration of acid becomes less

than 88 percent, some of the acid must be removed and replaced with stronger acid In the hydrofluoric acid process, the slip stream of acid is redistilled Dissolved polymerization products are removed from the acid as a thick dark oil The concentrated hydrofluoric acid is recycled and the net consumption is about 0 1 kilograms per barrel of alkylates produced Hydrofluoric acid alkylation units require special engineering design, operator training and safety equipment precautions to protect operators from accidental contact with hydrofluoric acid which is an extremely hazardous substance In the sulfuric acid process, the sulfuric acid removed must be regenerated in a sulfuric acid plant which is generally not a part of the alkylation unit and may be located off-site Spent sulfuric acid generation is substantial, typically in the range of 6 to 14 kilograms per barrel of alkylate Air emissions from the alkylation process may arise from process vents and fugitive emissions

4 3 1 2 7 Isomerization Isomerization is used to alter the arrangement of a molecule without adding or removing anything from the original molecule Typically, paraffins (butane or pentane from the crude distillation unit) are converted to isoparaffins having a much higher octane Isomerization reactions take place at temperatures in the range of 93 to 204°C in the presence of a catalyst that usually consists of platinum on a base material Two types of catalysts are currently in use One requires the continuous addition of small amounts of organic chlorides which are converted to hydrogen chloride in the reactor In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems The other type of catalyst uses a molecular sieve base and does not require a dry and oxygen free feed Both types of isomerization catalysts require an atmosphere of hydrogen to minimize coke deposits, however, the consumption of hydrogen is negligible Catalysts typically need to be replaced about every two to three years or longer Platinum is then recovered from the used catalyst off-site Light ends are stripped from the product stream leaving the reactor and are then sent to the sour gas treatment unit Some isomerization units utilize caustic treating of the light fuel gas stream to neutralize any entrained hydrochloric acid This will result in a calcium chloride (or other salts) waste stream Air emissions may arise from the process heater, vents and fugitive emissions Wastewater streams include caustic wash and sour water

4 3 1 2 8 Polymerization Polymerization is occasionally used to convert propene and butene to high octane gasoline blending components The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst The feed must be free of sulfur, which poisons the catalyst, basic materials, which neutralize the catalyst, and oxygen, which affects the reactions The propene and butene feed is washed first with caustic to remove mercaptans (molecules containing sulfur), then with an amine solution to remove hydrogen sulfide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer Air emissions of sulfur dioxide may arise during the caustic washing operation Spent catalyst, which typically is not regenerated, is occasionally disposed as a solid waste Wastewater streams will contain caustic wash and sour water with amines and mercaptans

4 3 1 2 9 Catalytic Reforming Catalytic reforming uses catalytic reactions to process primarily low octane heavy straight run (from the crude distillation unit) gasolines and naphthas into high octane aromatics (including benzene) There are four major types of reactions which occur during reforming processes 1) dehydrogenation of naphthenes to aromatics, 2)

dehydrocyclization of paraffins to aromatics, 3) isomerization, and 4) hydrocracking The dehydrogenation reactions are very endothermic, requiring that the hydrocarbon stream be heated between each catalyst bed All but the hydrocracking reaction release hydrogen which can be used in the hydrotreating or hydrocracking processes Fixed-bed or moving bed processes are utilized in a series of three to six reactors Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulfur, nitrogen and metallic contaminants In continuous reforming processes, catalysts can be regenerated one reactor at a time, once or twice per day, without disrupting the operation of the unit In semi-regenerative units, regeneration of all reactors can be carried out simultaneously after three to 24 months of operation by first shutting down the process

Air emissions from catalytic reforming arise from the process heater gas and fugitive emissions The catalysts used in catalytic reforming processes are usually very expensive and extra precautions are taken to ensure that catalyst is not lost When the catalyst has lost its activity and can no longer be regenerated, the catalyst is usually sent off-site for recovery of the metals Subsequent air emissions from catalyst regeneration is, therefore, relatively low Relatively small volumes of wastewater containing sulfides, ammonia, and mercaptans may be generated from the stripping tower used to remove light ends from the reactor effluent

4 3 1 2 10 Solvent Extraction Solvent extraction uses solvents to dissolve and remove aromatics from lube oil feed stocks, improving viscosity, oxidation resistance, color and gum formation A number of different solvents are used with the two most common being furfural and phenol Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disc contactor Each solvent has a different solvent-to-oil ratio and recycle ratio within the tower Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator The stream extracted from the solvent will likely contain high concentrations of hydrogen sulfide, aromatics, naphthenes and other hydrocarbons, and is often fed to the hydrocracking unit The water stream leaving the fractionator will likely contain some oil and solvents

4 3 1 2 11 Chemical Treating In petroleum refining, chemical treating is used to remove or change the undesirable properties associated with sulfur, nitrogen, or oxygen compound contaminates in petroleum products Chemical treating is accomplished by either extraction or oxidation (also known as sweetening), depending upon the product Extraction is used to remove sulfur from the very light petroleum fractions, such as propane/propylene (PP) and butane/butylene (BB) Sweetening, though, is more effective on gasoline and middle distillate products

A typical extraction process is "Merox" extraction Merox extraction is used to remove mercaptans (organic sulfur compounds) from PP and BB streams PP streams may undergo amine treating before the Merox extraction to remove excess H_2S which tends to fractionate with PP and interferes with the Merox process A caustic prewash of the PP and BB removes any remaining trace H_2S prior to Merox extraction

The PP and BB streams are passed up through the trays of an extraction tower Caustic solution flowing down the extraction tower absorbs mercaptan from the PP and BB streams The rich caustic is then regenerated by oxidizing the mercaptans to disulfide in the presence of aqueous

Merox catalyst and the lean caustic recirculated to the extraction tower The disulfide is insoluble in the caustic and can be separated

Oxidation or "sweetening" is used on gasoline and distillate fractions A common oxidation process is also a Merox process that uses a solid catalyst bed Air and a minimum amount of alkaline caustic ("mini-alky" operation) is injected into the hydrocarbon stream As the hydrocarbon passes through the Merox catalyst bed, sulfur mercaptans are oxidized to disulfide In the sweetening Merox process, the caustic is not regenerated The disulfide can remain with the gasoline product, since it does not possess the objectionable odor properties of mercaptans hence, the product has been "sweetened "

In the extraction process, a waste oily disulfide stream leaves the separator Air emissions arise from fugitive hydrocarbons and the process vents on the separator which may contain disulfides

4 3 1 2 12 De-waxing De-waxing of lubricating oil base stocks is necessary to ensure that the oil will have the proper viscosity at lower ambient temperatures Two types of de-waxing processes are used selective hydrocracking and solvent de-waxing In selective hydrocracking one or two zeolite catalysts are used to selectively crack the wax paraffins Solvent de-waxing is more prevalent In solvent de-waxing, the oil feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallized, and then filtered to remove the wax Solvents used for the process include propane and mixtures of methyl ethyl ketone (ME) with methyl isobutyl ketone (MICK) or ME with toluene Solvent is recovered from the oil and wax through heating, two-stage flashing, followed by steam stripping The solvent recovery stage results in solvent contaminated water which typically is sent to the wastewater treatment plant The wax is either used as feed to the catalytic cracker or is de-oiled and sold as industrial wax Air emissions may arise from fugitive emissions of the solvents

4 3 1 2 13 Propane De-asphalting Propane de-asphalting produces lubricating oil base stocks by extracting asphaltenes and resins from the residuals of the vacuum distillation unit Propane is usually used to remove asphaltenes due to its unique solvent properties At lower temperatures (38°-60°C), paraffins are very soluble in propane and at higher temperatures (about 93°C) all hydrocarbons are almost insoluble in propane The propane De-asphalting process is similar to solvent extraction in that a packed or baffled extraction tower or rotating disc contactor is used to mix the oil feed stocks with the solvent In the tower method, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower The oil, which is more soluble in the propane dissolves and flows to the top The asphaltene and resins flow to the bottom of the tower where they are removed in a propane mix Propane is recovered from the two streams through two-stage flash systems followed by steam stripping in which propane is condensed and removed by cooling at high pressure in the first stage and at low pressure in the second stage The asphalt recovered can be blended with other asphalts or heavy fuels, or can be used as feed to the coker The propane recovery stage results in propane contaminated water which typically is sent to the wastewater treatment plant Air emissions may arise from fugitive propane emissions and process vents

4 3 1 3 Supporting Operations Many important refinery operations are not directly involved in the production of hydrocarbon fuels but serve in a supporting role Some of the major supporting processes are discussed below

4 3 1 3 1 Wastewater Treatment Relatively large volumes of water are used by the petroleum refining industry Four types of wastewater are produced surface water runoff, cooling water, process water, and sanitary wastewater Surface water runoff is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains Runoff surface water also includes water coming from crude and product storage tank roof drains

A large portion of water used in petroleum refining is used for cooling Cooling water typically does not come into direct contact with process oil streams and therefore contains less contaminants than process wastewater Most cooling water is recycled over and over with a bleed or blowdown stream to the wastewater treatment unit to control the concentration of contaminants and the solids content in the water Cooling towers within the recycle loop cool the water using ambient air (see Storage Tanks and Cooling Towers) Some cooling water termed "once through," is passed through a process unit once and is then discharged directly without treatment in the wastewater treatment plant The water used for cooling often contains chemical additives such as chromates, phosphates, and anti-fouling biocides to prevent scaling of pipes and biological growth (It should be noted, however, that many refineries no longer use chromates in cooling water as anti-fouling agents) Although cooling water usually does not come into direct contact with oil process streams, it also may contain some oil contamination due to leaks in the process equipment

Water used in processing operations also accounts for a significant portion of the total wastewater Process wastewater arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown Because process water often comes into direct contact with oil, it is usually highly contaminated

Wastewater treatment plants are a significant source of refinery air emissions and solid wastes Air releases arise from fugitive emissions from the numerous tanks, ponds and discharge system drains Solid wastes are generated in the form of sludges from a number of the treatment units

4 3 1 3 2 Gas Treatment and Sulfur Recovery Process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units and hydroprocessing units can contain high concentrations of hydrogen sulfide mixed with light refinery fuel gases Before elemental sulfur can be recovered, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulfide This is typically accomplished by dissolving the hydrogen sulfide in a chemical solvent Solvents most commonly used are amines, such as diethanolamine (DEA) Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide are also used In the amine solvent processes, DEA solution or another amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulfide is dissolved in the solution The fuel gases are removed for use as fuel in process furnaces in other refinery operations The amine-hydrogen sulfide solution is then heated and steam stripped to remove the hydrogen sulfide gas

Current methods for removing sulfur from the hydrogen sulfide gas streams are typically a combination of two processes the Claus Process followed by the Beaven Process, Scot Process, or the Wellman-Land Process The Claus process consists of partial combustion of the hydrogen

sulfide-rich gas stream (with one-third the stoichiometric quantity of air) and then reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur

Since the Claus process by itself removes only about 90 percent of the hydrogen sulfide in the gas stream, the Beaven, Scot, or Wellman-Lord processes are often used to further recover sulfur In the Beaven process, the hydrogen sulfide in the relatively low concentration gas stream from the Claus process can be almost completely removed by absorption in a quinone solution The dissolved hydrogen sulfide is oxidized to form a mixture of elemental sulfur and hydro-quinone The solution is injected with air or oxygen to oxidize the hydro-quinone back to quinone The solution is then filtered or centrifuged to remove the sulfur and the quinone is then reused The Beaven process is also effective in removing small amounts of sulfur dioxide, carbonyl sulfide, and carbon disulfide that are not affected by the Claus process These compounds are first converted to hydrogen sulfide at elevated temperatures in a cobalt molybdate catalyst prior to being fed to the Beaven unit Air emissions from sulfur recovery units will consist of hydrogen sulfide, SO_x and NO_x in the process tail gas as well as fugitive emissions and releases from vents

The Scot process is also widely used for removing sulfur from the Claus tail gas The sulphur compounds in the Claus tail gas are converted to hydrogen sulfide by heating and passing it through a cobalt-molybdenum catalyst with the addition of a reducing gas The gas is then cooled and contacted with a solution of di-isopropanolamine (DIPA) which removes all but trace amounts of hydrogen sulfide The sulfide-rich DIPA is sent to a stripper where hydrogen sulfide gas is removed and sent to the Claus plant The DIPA is returned to the absorption column

4 3 1 3 3 Additive Production A number of chemicals (mostly alcohols and ethers) are added to motor fuels to improve performance

The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), and tertiary amyl methyl ether (TAME) Many of the larger refineries manufacture their own supplies of MTBE and TAME by reacting isobutylene and/or isoamylene with methanol Smaller refineries usually buy their supplies from chemical manufacturers or the larger refineries Isobutylene is obtained from a number of refinery sources including the light naphtha from the FCCU and coking units, the by-product from steam cracking of naphtha or light hydrocarbons during the production of ethylene and propylene, catalytic dehydrogenation of isobutane, and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides Several different processes are currently in use to produce MTBE and TAME from isobutylene and methanol Most processes use a two-stage acidic ion exchange resin catalyst The reaction is exothermic and cooling to the proper reaction temperature is critical in obtaining the optimal conversion efficiency The process usually produces an MTBE or TAME stream and a relatively small stream of unreacted hydrocarbons and methanol The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling

4 3 1 3 4 Heat Exchanger Cleaning Heat exchangers are used throughout petroleum refineries to heat or cool petroleum process streams The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream The bundles are cleaned periodically to remove

accumulations of scales, sludge and any oily residues Because chromium has almost been eliminated as a cooling water additive, wastes generated from the cleaning of heat exchanger bundles no longer account for a significant portion of the hazardous wastes generated at refining facilities The sludge generated may contain lead or chromium, although some refineries which do not produce leaded gasoline and which use non-chrome corrosion inhibitors typically do not generate sludge that contains these constituents Oily wastewater is also generated during heat exchanger cleaning

4 3 1 3 5 Blowdown System Most refinery process units and equipment are manifolded into a collection unit, called the blowdown system Blowdown systems provide for the safe handling and disposal of liquid and gases that are either automatically vented from the process units through pressure relief valves, or that are manually drawn from units Recirculated process streams and cooling water streams are often manually purged to prevent the continued build up of contaminants in the stream Part or all of the contents of equipment can also be purged to the blowdown system prior to shutdown before normal or emergency shutdowns Blowdown systems utilize a series of flash drums and condensers to separate the blowdown into its vapor and liquid components The liquid is typically composed of mixtures of water and hydrocarbons containing sulfides, ammonia, and other contaminants, which are sent to the wastewater treatment plant The gaseous component typically contains hydrocarbons, hydrogen sulfide, ammonia, mercaptans, solvents, and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulfur oxides when flared

4 3 1 3 6 Blending Blending is the final operation in petroleum refining It consists of mixing the products in various proportions to meet specifications such as vapor pressure, specific gravity, sulfur content, viscosity, octane number, cetane index, initial boiling point, and pour point Blending can be carried out in-line or in batch blending tanks Air emissions from blending are fugitive volatile organic compounds (VOCs) from blending tanks, valves, pumps and mixing operations

4 3 1 3 7 Storage Tanks Storage tanks are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing Finished petroleum products are also kept in storage tanks before transport off site Storage tank bottoms are mixtures of iron rust from corrosion, sand, water, and emulsified oil and wax, which accumulate at the bottom of tanks Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued build up

Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks

4 3 1 3 8 Cooling Towers Cooling towers cool heated water by circulating the water through a tower with a predetermined flow of ambient air pushed with large fans A certain amount of water exits the system through evaporation, mist droplets and as bleed or blowdown to the wastewater treatment system Therefore, make-up water in the range of about five percent of the circulation rate is required

4 3 2 Raw Material Inputs and Pollution Outputs in the Production Line

Raw material input to petroleum refineries is primarily crude oil, however, petroleum refineries use and generate an enormous number of chemicals, many of which leave the facilities as discharges of air emissions, wastewater, or solid waste Pollutants generated typically include VOCs, carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH_3), hydrogen sulfide (H_2S), metals, spent acids, and numerous toxic organic compounds Exhibit 4-1 summarizes the main pollutant outputs for each major refinery process

When discussing material outputs of the petroleum refining industry, it is important to note the relationship between the outputs of the industry itself and the outputs resulting from the use of refinery products The pollutant outputs from the refining facilities are modest in comparison to the pollutant outputs realized from the consumption of petroleum products by the transportation sector, electric utilities, chemical manufacturers and other industrial and commercial users

4 3 2 1 Air Emissions Air emissions from refineries include fugitive emissions of the volatile constituents in crude oil and its fractions, emissions from the burning of fuels in process heaters and emissions from the various refinery processes themselves Fugitive emissions occur throughout refineries and arise from the thousands of potential fugitive emission sources such as valves, pumps, tanks, pressure relief valves, flanges, etc While individual leaks are typically small, the sum of all fugitive leaks at a refinery can be one of its largest emission sources Fugitive emissions can be reduced through a number of techniques, including improved leak resistant equipment, reducing the number of tanks and other potential sources and, perhaps the most effective method, an ongoing leak detection and repair program

The numerous process heaters used in refineries to heat process streams or to generate steam (boilers) for heating or steam stripping can be potential sources of SO_x, NO_x, CO, particulates and hydrocarbons emissions When operating properly and when burning cleaner fuels such as refinery fuel gas, fuel oil or natural gas, these emissions are relatively low If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significant

The majority of gas streams exiting each refinery process contain varying amounts of refinery fuel gas, hydrogen sulfide and ammonia These streams are collected and sent to the gas treatment and sulfur recovery units to recover the refinery fuel gas and sulfur Emissions from the sulfur recovery unit typically contains some H_2S, SO_x and NO_x Other emissions sources from refinery processes arise from periodic regeneration of catalysts These processes generate streams that may contain relatively high levels of carbon monoxide, particulates and VOCs Before being discharged to the atmosphere, such off-gas streams may be treated first through a carbon monoxide boiler to burn carbon monoxide and any VOCs, and then through an electrostatic precipitator or cyclone separator to remove particulates

4 3 2 2 Wastewater Wastewaters consist of cooling water, process water, sanitary sewage water, and storm water

Many refineries unintentionally release, or have unintentionally released in the past, liquid hydrocarbons to ground water and surface waters At some refineries, contaminated ground

water has migrated off-site and resulted in continuous "seeps" to surface waters There is the potential to contaminate large volumes of ground water and surface water possibly posing a substantial risk to human health and the environment

Other Wastes Other hazardous and non-hazardous wastes are generated from many of the refining processes, petroleum handling operations, as well as wastewater treatment Residual refinery wastes are typically in the form of sludges, spent process catalysts, filter clay, and incinerator ash Treatment of these wastes includes incineration, land treating off-site, land filling on-site, land filling off-site, chemical fixation, neutralization, and other treatment methods

A significant portion of the non-petroleum product outputs of refineries is typically transported off-site and sold as byproducts These outputs include sulfur, acetic acid, phosphoric acid, and recovered metals Metals from catalysts and from the crude oil that have deposited on the catalyst during the production often are recovered by third party recovery facilities

Exhibit 4-1 Typical Material Outputs from Selected Petroleum Refining Processes

Process	Air Emissions	Process Waste Water	Residual Wastes Generated
Crude oil desalting	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) fugitive emissions (hydrocarbons)	Flow=2 1 Gal/Bbl Oil H_2S NH_3 phenol high levels of suspended solids dissolved solids high BOD high temperature	Crude oil/desalter sludge (iron rust, clay sand water emulsified oil and wax metals)
Atmospheric distillation	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) vents and fugitive emissions (hydrocarbons)	Flow=26 0 Gal/Bbl Oil H_2S NH_3 suspended solids chlorides mercaptans phenol elevated pH	Typically little or no residual waste generated
Vacuum distillation	Steam ejector emissions (hydrocarbons) heater stack gas (CO SO_x NO_x hydrocarbons and particulates) vents and fugitive emissions (hydrocarbons)		
Thermal cracking/ visbreaking	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) vents and fugitive emissions (hydrocarbons)	Flow=2 0 Gal/Bbl Oil H_2S NH_3 phenol suspended solids high pH BOD_5 COD	Typically little or no residual waste generated
Coking	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) vents and fugitive emissions (hydrocarbons) and decoking emissions (hydrocarbons and particulates)	Flow=1 0 Gal/Bbl High pH H_2S NH_3 suspended solids COD	Coke dust (carbon particles and hydrocarbons)
Catalytic cracking	Heater stack gas (CO SO NO_x hydrocarbons and particulates) fugitive emissions (hydrocarbons) and catalyst regeneration (CO NO_x SO and particulates)	Flow=15 0 Gal/Bbl High levels of oil suspended solids phenols cyanides H_2S NH_3 high pH BOD COD	Spent catalysts (metals from crude oil and hydrocarbons) spent catalyst fines from electrostatic precipitators (aluminum silicate and metals)
Catalytic hydro cracking	Heater stack gas (CO SO NO hydrocarbons and particulates) fugitive emissions (hydrocarbons) and catalyst regeneration (CO NO_x SO_x and catalyst dust)	Flow=2 0 Gal/Bbl High COD suspended solids H_2S relatively low levels of BOD	Spent catalysts fines (metals from crude oil and hydrocarbons)

Process	Air Emissions	Process Waste Water	Residual Wastes Generated
Hydrotreating/ hydroprocessing	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) vents and fugitive emissions (hydrocarbons) and catalyst regeneration (CO NO SO_x)	Flow=1 0 Gal/Bbl H_2S NH_3 High pH phenols suspended solids BOD COD	Spent catalyst fines (aluminum silicate and metals)
Alkylation	Heater stack gas (CO SO NO hydrocarbons and particulates) vents and fugitive emissions (hydrocarbons)	Low pH suspended solids dissolved solids COD H_2S spent sulfuric acid	Neutralized alkylation sludge (sulfuric acid or calcium fluoride hydrocarbons)
Isomerization	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) HCl (potentially in light ends) vents and fugitive emissions (hydrocarbons)	Low pH chloride salts caustic wash relatively low H_2S and NH_3	Calcium chloride sludge from neutralized HCl gas
Polymerization	H_2S from caustic washing	H_2S NH_3 caustic wash mercaptans and ammonia, high pH	Spent catalyst containing phosphoric acid
Catalytic reforming	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) fugitive emissions (hydrocarbons) and catalyst regeneration (CO NO SO_x)	Flow=6 0 Gal/Bbl High levels oil suspended solids COD Relatively low H_2S	Spent catalyst fines from electrostatic precipitators (alumina silicate and metals)
Solvent extraction	Fugitive solvents	Oil and solvents	Little or no residual wastes generated
Dewaxing	Fugitive solvents, heaters	Oil and solvents	Little or no residual wastes generated
Propane deasphalting	Heater stack gas (CO SO_x NO_x hydrocarbons and particulates) fugitive propane	Oil and propane	Little or no residual wastes generated
Merox treating	Vents and fugitive emissions (hydrocarbons and disulfides)	Little or no wastewater generated	Spent Merox caustic solution waste oil disulfide mixture
Wastewater treatment	Fugitive emissions (H_2S NH_3 and hydrocarbons)	Not applicable	API separator sludge (phenols metals and oil) chemical precipitation sludge (chemical coagulants oil) DAF floats biological sludges (metals oil suspended solids) spent lime
Gas treatment and sulfur recovery	SO_x NO_x and H_2S from vent and tail gas emissions	H_2S NH_3 amines Stretford solution	Spent catalyst

Process	Air Emissions	Process Waste Water	Residual Wastes Generated
Blending	Fugitive emissions (hydrocarbons)	Little or no wastewater generated	Little or no residual waste generated
Heat exchanger cleaning	Periodic fugitive emissions (hydrocarbons)	Oily wastewater generated	Heat exchanger sludge (oil metals and suspended solids)
Storage tanks	Fugitive emissions (hydrocarbons)	Water drained from tanks contaminated with tank product	Tank bottom sludge (iron rust, clay sand water emulsified oil and wax metals)
Blowdown and flare	Combustion products (CO SO_x NO_x and hydrocarbons) from flares, fugitive emissions	Little or no wastewater generated	Little or no residual waste generated

4 4 Summary of Health and Toxicity Effects of Selected Chemicals Associated with Petroleum Refining

4 4 1 Ammonia

Sources Ammonia is formed from the nitrogen bearing components of crude oil and can be found throughout petroleum refineries in both the gaseous and aqueous forms Gaseous ammonia often leaves distillation, cracking and treating processes mixed with the sour gas or acid gas along with refinery fuel gases and hydrogen sulfide Aqueous ammonia is present in the sour water generated in the vacuum distillation unit and steam strippers or fractionators Some release sources include, fugitive emissions, sour gas stripper, sulfur unit and wastewater discharges

Toxicity Anhydrous ammonia is irritating to the skin, eyes, nose, throat, and upper respiratory system

Ecologically, ammonia is a source of nitrogen (an essential element for aquatic plant growth), and may therefore contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters In addition, aqueous ammonia is moderately toxic to aquatic organisms

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Ammonia combines with sulfate ions in the atmosphere and is washed out by rainfall, resulting in rapid return of ammonia to the soil and surface waters Ammonia is a central compound in the environmental cycling of nitrogen Ammonia in lakes, rivers, and streams is converted to nitrate

Physical Properties Ammonia is a corrosive and severely irritating gas with a pungent odor

4 4 2 Toluene

Sources Toluene is a component of crude oil and is therefore present in many refining operations Toluene is also produced during catalytic reforming and is sold as one of the large volume aromatics used as feedstocks in chemical manufacturing Its volatile nature makes fugitive emissions its largest release source Point air sources may arise during the process of separating toluene from other aromatics and from solvent de-waxing operations where toluene is often used as the solvent

Toxicity Inhalation or ingestion of toluene can cause headaches, confusion, weakness and memory loss Toluene may also affect the way the kidneys and liver function

Reactions of toluene (see environmental fate) in the atmosphere contribute to the formation of ozone in the lower atmosphere Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers

Some studies have shown that unborn animals were harmed when high levels of toluene were inhaled by their mothers, although the same effects were not seen when the mothers were fed large quantities of toluene Note that these results may reflect similar difficulties in humans
Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate A portion of releases of toluene to land and water will evaporate Toluene may also be degraded by microorganisms Once volatilized, toluene in the lower atmosphere will react with other atmospheric components contributing to the formation of ground-level ozone and other air pollutants

Physical Properties Toluene is a volatile organic chemical

4 4 3 Xylenes (Mixed Isomers)

Sources Xylene isomers are a component of crude oil and are therefore present in many refining operations Xylenes are also produced during catalytic reforming and are sold as one of the large volume aromatics used as feedstocks in chemical manufacturing Xylene's volatile nature make fugitive emissions the largest release source Point air sources may arise during the process of separating xylene from other aromatics

Toxicity Xylenes are rapidly absorbed into the body after inhalation, ingestion, or skin contact Short-term exposure of humans to high levels of xylene can cause irritation of the skin, eyes, nose, and throat, difficulty in breathing, impaired lung function, impaired memory, and possible changes in the liver and kidneys Both short- and long-term exposure to high concentrations can cause effects such as headaches, dizziness, confusion, and lack of muscle coordination Reactions of xylene (see environmental fate) in the atmosphere contribute to the formation of ozone in the lower atmosphere Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate A portion of releases to land and water will quickly evaporate, although some degradation by microorganisms will occur

Xylenes are moderately mobile in soils and may leach into groundwater, where they may persist for several years

Xylenes are volatile organic chemicals As such, xylene in the lower atmosphere will react with other atmospheric components, contributing to the formation of ground-level ozone and other air pollutants

4 4 4 Methyl Ethyl Ketone

Sources Methyl ethyl ketone (ME or MEK) is used in some refineries as a solvent in lube oil de-waxing Its extremely volatile characteristic makes fugitive emissions its primary source of releases to the environment

Toxicity Breathing moderate amounts of methyl ethyl ketone (ME) for short periods of time can cause adverse effects on the nervous system ranging from headaches, dizziness, nausea, and numbness in the fingers and toes to unconsciousness Its vapors are irritating to the skin, eyes, nose, and throat and can damage the eyes Repeated exposure to moderate to high amounts may cause liver and kidney effects

Carcinogenicity No agreement exists over the carcinogenicity of ME One source believes ME is a possible carcinogen in humans based on limited animal evidence Other sources believe that there is insufficient evidence to make any statements about possible carcinogenicity

Environmental Fate Most of the ME released to the environment will end up in the atmosphere ME can contribute to the formation of air pollutants in the lower atmosphere It can be degraded by microorganisms living in water and soil

Physical Properties Methyl ethyl ketone is a flammable liquid

4 4 5 Propylene

Sources Propylene (propene) is one of the light ends formed during catalytic and thermal cracking and coking operations It is usually collected and used as a feedstock to the alkylation unit Propylene is volatile and soluble in water making releases to both air and water significant

Toxicity At low concentrations, inhalation of propylene causes mild intoxication, a tingling sensation, and an inability to concentrate At higher concentrations, unconsciousness, vomiting, severe vertigo, reduced blood pressure, and disordered heart rhythms may occur Skin or eye contact with propylene causes freezing burns

Reaction of propylene (see environmental fate) in the atmosphere contributes to the formation of ozone in the lower atmosphere Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers

Ecologically, similar to ethylene, propylene has a stimulating effect on plant growth at low concentrations, but inhibits plant growth at high levels

Carcinogenicity There is currently no evidence to suggest that this chemical is carcinogenic

Environmental Fate Propylene is degraded principally by hydroxyl ions in the atmosphere Propylene released to soil and water is removed primarily through volatilization Hydrolysis, bioconcentration, and soil adsorption are not expected to be significant fate processes of propylene in soil or aquatic ecosystems Propylene is readily biodegraded by microorganisms in surface water

Physical Properties Propylene is a volatile organic chemical

4 4 6 Benzene

Sources Benzene is a component of crude oil and is therefore present in many refining operations Benzene is also produced during catalytic reforming and is sold as one of the large volume aromatics used as feedstocks in chemical manufacturing Benzene's volatile nature makes fugitive emissions the largest release source Point air sources may arise during the process of separating benzene from other aromatics

Toxicity Short-term inhalation of benzene primarily affects the central nervous system and respiratory system Chronic exposure to benzene causes bone marrow toxicity in animals and humans, causing suppression of the immune system and development of leukemia Ingestion of benzene is rare

Reactions of benzene (see environmental fate) in the atmosphere contributes to the formation of ozone in the lower atmosphere (troposphere) Ozone can affect the respiratory system, especially in sensitive individuals such as asthma or allergy sufferers

Carcinogenicity Benzene is a known human carcinogen, based on both oral and inhalation exposures

Environmental Fate A portion of benzene releases to soil and surface waters evaporate rapidly Benzene is highly mobile in the soil and may leach to groundwater Once in groundwater, it is likely biodegraded by microorganisms only in the presence of oxygen

Benzene is not expected to significantly adsorb to sediments, bioconcentrate in aquatic organisms, or break down in water Atmospheric benzene is broken down through reacting with chemical ions in the air, this process is greatly accelerated in the presence of other air pollutants such as nitrogen oxides or sulfur dioxide Benzene is fairly soluble in water and is removed from the atmosphere in rain

As a volatile chemical, benzene in the lower atmosphere will react with other atmospheric components, contributing to the formation of ground-level ozone and other air pollutants, which can contribute to respiratory illnesses in both the general and highly susceptible populations, such as asthmatics and allergy-sufferers

4 5 Pollution Prevention Opportunities

This section provides both general and company-specific descriptions of some pollution prevention advances that have been implemented within the petroleum refining industry While the list is not exhaustive, it does provide core information that can be used as the starting point for facilities interested in beginning their own pollution prevention projects Please note that the activities described in this section do not necessarily apply to all facilities that fall within this sector Facility-specific conditions must be carefully considered when pollution prevention options are evaluated, and the full impacts of the change must examine how each option affects air, land, and water pollutant releases

It should be emphasized that source reduction is the best pollution prevention measure in every case When source reduction opportunities have been exhausted, recycling, treatment, and disposal measures should be considered (in that order) Although this section presents viable product recycling options, implementers of pollution prevention measures should be aware that recycling, treatment, and disposal options will typically be more expensive in the long term

4 5 1 Opportunities from Process/Equipment Modifications

4 5 1 1 Place Secondary Seals on Storage Tanks One of the largest sources of fugitive emissions from refineries is storage tanks containing gasoline and other volatile products These losses can be significantly reduced by installing secondary seals on storage tanks

4 5 1 2 Establish Leak Detection and Repair Program Fugitive emissions are one of the largest sources of refinery hydrocarbon emissions A leak detection and repair program consists of using a portable VOC detecting instrument to detect leaks during regularly scheduled inspections of valves, flanges, and pump seals Leaks are then repaired immediately or are scheduled for repair as quickly as possible A leak detection and repair program could reduce fugitive emissions 40 to 64 percent, depending on the frequency of inspections

4 5 1 3 Regenerate or Eliminate Filtration Clay Clay from refinery filters must periodically be replaced Spent clay often contains significant amounts of entrained hydrocarbons and, therefore, must be designated as hazardous waste Back washing spent clay with water or steam can reduce the hydrocarbon content to levels so that it can be reused or handled as a nonhazardous waste Another method used to regenerate clay is to wash the clay with naphtha, dry it by steam heating and then feed it to a burning kiln for regeneration In some cases clay filtration can be replaced entirely with hydrotreating

4 5 1 4 Reduce the Generation of Tank Bottoms Tank bottoms from crude oil storage tanks constitute a large percentage of refinery solid waste and pose a particularly difficult disposal problem due to the presence of heavy metals Tank bottoms are comprised of heavy hydrocarbons, solids, water, rust and scale Minimization of tank bottoms is carried out most cost effectively through careful separation of the oil and water remaining in the tank bottom Filters and centrifuges can also be used to recover the oil for recycling

4 5 1 5 Minimize Solids Leaving the Desalter Solids entering the crude distillation unit are likely to eventually attract more oil and produce additional emulsions and sludges The amount

of solids removed from the desalting unit should, therefore, be maximized A number of techniques can be used such as using low shear mixing devices to mix desalter wash water and crude oil, using lower pressure water in the desalter to avoid turbulence, and replacing the water jets used in some refineries with mud rakes which add less turbulence when removing settled solids

4 5 1 6 Minimize Cooling Tower Blowdown The dissolved solids concentration in the recirculating cooling water is controlled by purging or blowing down a portion of the cooling water stream to the wastewater treatment system Solids in the blowdown eventually create additional sludge in the wastewater treatment plant However, the amount of cooling tower blowdown can be lowered by minimizing the dissolved solids content of the cooling water A significant portion of the total dissolved solids in the cooling water can originate in the cooling water makeup stream in the form of naturally occurring calcium carbonates Such solids can be controlled either by selecting a source of cooling tower makeup water with less dissolved solids or by removing the dissolved solids from the makeup water stream Common treatment methods include cold lime softening, reverse osmosis, or electrodialysis

4 5 1 7 Install Vapor Recovery for Barge Loading Although barge loading is not a factor for all refineries, it is an important emissions source for many facilities It is estimated that these emissions could be reduced 98 percent by installing a marine vapor loss control system Such systems could consist of vapor recovery or VOC destruction in a flare

4 5 1 8 Minimize FCCU Decant Oil Sludge Decant oil sludge from the fluidized bed catalytic cracking unit (FCCU) can contain significant concentrations of catalyst fines These fines often prevent the use of decant oil as a feedstock or require treatment which generates an oily catalyst sludge Catalysts in the decant oil can be minimized by using a decant oil catalyst removal system One system incorporates high voltage electric fields to polarize and capture catalyst particles in the oil The amount of catalyst fines reaching the decant oil can be minimized by installing high efficiency cyclones in the reactor to shift catalyst fines losses from the decant oil to the regenerator where they can be collected in the electrostatic precipitator

4 5 1 9 Control of Heat Exchanger Cleaning Solids In many refineries, using high pressure water to clean heat exchanger bundles generates and releases water and entrained solids to the refinery wastewater treatment system Exchanger solids may then attract oil as they move through the discharge system and may also produce finer solids and stabilized emulsions that are more difficult to remove Solids can be removed at the heat exchanger cleaning pad by installing concrete overflow weirs around the surface drains or by covering drains with a screen Other ways to reduce solids generation are by using anti-foulants on the heat exchanger bundles to prevent scaling and by cleaning with reusable cleaning chemicals that also allow for the easy removal of oil

4 5 1 10 Control of Surfactants in Wastewater Surfactants entering the refinery wastewater streams will increase the amount of emulsions and sludges generated Surfactants can enter the system from a number of sources including washing unit pads with detergents, treating gasolines with an end point over 204°C thereby producing spent caustics, cleaning tank truck tank interiors, and using soaps and cleaners for miscellaneous tasks In addition, the overuse and mixing of the organic polymers used to separate oil, water and solids in the wastewater treatment

plant can actually stabilize emulsions The use of surfactants should be minimized by educating operators, routing surfactant sources to a point downstream of the DAF unit and by using dry cleaning, high pressure water or steam to clean oil surfaces of oil and dirt

4 5 1 11 Thermal Treatment of Applicable Sludges The toxicity and volume of some de-oiled and de-watered sludges can be further reduced through thermal treatment Thermal sludge treatment units use heat to vaporize the water and volatile components in the feed and leave behind a dry solid residue The vapors are condensed for separation into the hydrocarbon and water components Non-condensable vapors are either flared or sent to the refinery amine unit for treatment and use as refinery fuel gas

4 5 1 12 Eliminate Use of Open Ponds Open ponds used to cool, settle out solids and store process water can be a significant source of VOC emissions Wastewater from coke cooling and coke VOC removal is occasionally cooled in open ponds where VOCs easily escape to the atmosphere In many cases, open ponds can be replaced with closed storage tanks

4 5 1 13 Remove Unnecessary Storage Tanks from Service Since storage tanks are one of the largest sources of VOC emissions, a reduction in the number of these tanks can have a significant impact The need for certain tanks can often be eliminated through improved production planning and more continuous operations By minimizing the number of storage tanks, tank bottom solids and decanted wastewater may also be reduced

4 5 1 14 Replace Old Boilers Older refinery boilers can be a significant source of SO_x, NO_x and particulate emissions It is possible to replace a large number of old boilers with a single new co-generation plant with emissions controls

4 5 1 15 Modify the FCCU to Allow the Use of Catalyst Fines Some FCCUs can be modified to recycle some of the catalyst fines generated

4 5 1 16 Reduce the Use of 55-gallon Drums Replacing 55-gallon drums with bulk storage can minimize the chances of leaks and spills

4 5 1 17 Install Rupture Discs and Plugs Rupture discs on pressure relieve valves and plugs in open ended valves can reduce fugitive emissions

4 5 1 18 Install High Pressure Power Washer Chlorinated solvent vapor degreasers can be replaced with high pressure power washers which do not generate spent solvent hazardous wastes

4 5 1 19 Refurbish or Eliminate Underground Piping Underground piping can be a source of undetected releases to the soil and groundwater Inspecting, repairing or replacing underground piping with surface piping can reduce or eliminate these potential sources

4 5 2 Opportunities from Material Substitution

4 5 2 1 Use Non-hazardous Degreasers Spent conventional degreaser solvents can be reduced or eliminated through substitution with less toxic and/or biodegradable products

4 5 2 2 Eliminate Chromates as an Anti-corrosive Chromate containing wastes can be reduced or eliminated in cooling tower and heat exchanger sludges by replacing chromates with less toxic alternatives such as phosphates

4 5 2 3 Use High Quality Catalysts By using catalysts of a higher quality, process efficiencies can be increased while the required frequency of catalyst replacement can be reduced

4 5 2 4 Replace Ceramic Catalyst Support with Activated Alumina Supports Activated alumina supports can be recycled with spent alumina catalyst

4 5 3 Opportunities from Recycling

4 5 3 1 Recycle and Regenerate Spent Caustics Caustics used to absorb and remove hydrogen sulfide and phenol contaminants from intermediate and final product streams can often be recycled Spent caustics may be saleable to chemical recovery companies if concentrations of phenol or hydrogen sulfide are high enough Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make recovery of the contaminants economical Caustics containing phenols can also be recycled on-site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation The caustic can then be treated in the refinery wastewater system

4 5 3 2 Use Oily Sludges as Feedstock Many oily sludges can be sent to a coking unit or the crude distillation unit where it becomes part of the refinery products Sludge sent to the coker can be injected into the coke drum with the quench water, injected directly into the delayed coker, or injected into the coker blowdown contactor used in separating the quenching products Use of sludge as a feedstock has increased significantly in recent years and is currently carried out by most refineries The quantity of sludge that can be sent to the coker is restricted by coke quality specifications which may limit the amount of sludge solids in the coke Coking operations can be upgraded, however, to increase the amount of sludge that they can handle

4 5 3 3 Control and Reuse FCCU and Coke Fines Significant quantities of catalyst fines are often present around the FCCU catalyst hoppers and reactor and regeneration vessels Coke fines are often present around the coker unit and coke storage areas The fines can be collected and recycled before being washed to the discharge system or migrating off-site via the wind Collection techniques include dry sweeping the catalyst and coke fines and sending the solids to be recycled or disposed of as non-hazardous waste Coke fines can also be recycled for fuel use Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse for collection

4 5 3 4 Recycle Lab Samples Lab samples can be recycled to the oil recovery system

4 5 4 Opportunities from Waste Segregation and Separation

Waste segregation and separation activities are not technically considered pollution prevention (since the waste has been generated as opposed to prevented) However, the advantage of separating highly toxic wastes from less toxic ones is that the possibility that *all* of the waste will pose serious health and environmental consequences is substantially minimized

4 5 4 1 Segregate Process Waste Streams A significant portion of refinery waste arises from oily sludges found in combined process/storm drainage systems Segregation of the relatively clean rainwater runoff from the process streams can reduce the quantity of oily sludges generated Furthermore, there is a much higher potential for recovery of oil from smaller, more concentrated process streams

4 5 4 2 Control Solids Discharge Systems Solids released to the wastewater discharge system can account for a large portion of a refinery's oily sludges Solids entering the discharge system (primarily soil particles) become coated with oil and are deposited as oily sludges in the oil/water separator Because a typical sludge has a solids content of five to 30 percent by weight, preventing one pound of solids from entering the discharge system can eliminate one to 9 kilograms of oily sludge Methods used to control solids include using a street sweeper on paved areas, paving unpaved areas, planting ground cover on unpaved areas, re-lining discharge systems, cleaning solids from ditches and catch basins, and reducing heat exchanger bundle cleaning solids by using anti-foulants in cooling water

4 5 4 3 Improve Recovery of Oils from Oily Sludges Because oily sludges make up a large portion of refinery solid wastes, any improvement in the recovery of oil from the sludges can significantly reduce the volume of waste There are a number of technologies currently in use to mechanically separate oil, water and solids, including belt filter presses, recessed chamber pressure filters, rotary vacuum filters, scroll centrifuges, disc centrifuges, shakers, thermal driers and centrifuge-drier combinations

4 5 4 4 Identify Benzene Sources and Install Upstream Water Treatment Benzene in wastewater can often be treated more easily and effectively at the point it is generated rather than at the wastewater treatment plant after it is mixed with other wastewater

4 5 5 Drivers and Barriers to Pollution Prevention in the Petroleum Refining Industry

For the petroleum refining industry, pollution prevention will primarily be realized through improved operating procedures, increased recycling, and process modifications

Although numerous cases have been documented where petroleum refineries have simultaneously reduced pollution outputs and operating costs through pollution prevention techniques, there are often barriers to their implementation The primary barrier to most pollution prevention projects is cost Many pollution prevention options simply do not pay for themselves Corporate investments typically must earn an adequate return on invested capital for the shareholders and some pollution prevention options at some facilities may not meet the requirements set by the companies In addition, the equipment used in the petroleum refining industry are very capital intensive and have very long lifetimes This reduces the incentive to make process modifications to (expensive) installed equipment that is still useful It should be noted that pollution prevention techniques are, nevertheless, often more cost-effective than pollution reduction through end-of-pipe treatment

APPENDIX 1

CHEMICAL POLLUTION PREVENTION CASE STUDIES

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PROFILES IN PREVENTION

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COURTESY OF THE CHEMICAL MANUFACTURER'S ASSOCIATION

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POLLUTION 450 million pounds a year of spent sulfuric acid was disposed of by deepwell injection.

PREVENTION A regeneration plant was built to produce sulfuric acid for re-use and sale.

Recycling Sulfuric Acid — I

Sulfuric acid is one of the most common chemicals in the world. It is used to make a myriad of products that improve the quality of life. Sulfuric acid in batteries enables cars to start every morning. It is used in refining gasoline and in making steel.

However, the acid sometimes ends up as waste that has to be disposed of. It may be impure or the wrong strength or there is no economic use for it.

At Cytec Industries' Fortier plant in Westwego, Louisiana, the production process for methyl methacrylate — or MMA — an intermediate chemical used in the manufacture of acrylic plastics — generated roughly 150 million pounds a year of spent acid that was disposed of via deepwell injection.

During the 1970s, Cytec began looking at alternatives to deepwell injection. This effort expanded in 1981 when Cytec formed a team to research ways to reduce the spent acid, along with other streams. The team came up with four possible alternatives to reduce the waste acid:

- Ammonium sulfate production: Spent acid could be used as a feedstock in the production of ammonium sulfate.
- Use of acid in phosphoric acid and diammonium phosphate production: Spent acid could be used to digest phosphate rock and produce either phosphoric acid or diammonium phosphate.
- Membrane technology: Membranes could be used to remove impurities to make the acid more usable; and
- Regeneration: Spent acid could be used as a feedstock in the production of virgin sulfuric acid.

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Within the first four months of start-up in 1994, the plant regenerated more than 9 million pounds of spent acid into usable sulfuric acid which was used in other plant processes or sold.

The team felt that regeneration offered the greatest promise to reduce the spent acid. Technical feasibility studies over the course of four years confirmed this. Based on success of the research, a $3.6 million project was undertaken in 1992 to convert an existing sulfur burning sulfuric acid plant at Fortier to a regeneration plant that could handle the spent acid. A new furnace, boiler and gas cleaning system are central elements of the recovery process.

Within the first four months of start-up in 1994 the plant regenerated more than nine million pounds of spent acid into usable sulfuric acid which was used in other plant processes or sold. This recycling effort alone will enable the Fortier plant to reduce its TRI emissions by 75 percent.

The sulfuric acid regeneration plant is only one of several ambitious waste reduction projects initiated by the Fortier plant. Cytec also built a facility capable of annually recovering up to 12 million pounds of acetonitrile and over one million pounds of hydrogen cyanide from deep well disposal and replaced the stripper column in the acrylonitrile facility which improved operations and reduced the hazardous process water and effluent discharge to the deep wells by 570 million pounds a year. In addition, the company plans to add a third process waste gas to-steam generator to provide complete destruction of organic vapor releases from the acrylonitrile process at the plant.

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ACID TO ACID, WASTE TO WASTE

POLLUTION An acid regeneration plant itself produced acid wastewater.

PREVENTION A study of furnace variables led to understanding how the waste was generated and how to cut the amount by 75 percent.

Recycling Sulfuric Acid — II

Rhone Poulenc is in the business of recycling sulfuric acid. Its Dominguez California plant takes used acid from nearby oil refineries and restores it to like new condition for resale.

The process involves burning the waste acid together with sulfur in an industrial furnace. The gases — principally sulfur dioxide — are cooled, cleaned and further processed to produce commercial grade sulfuric acid. During the process, weak sulfuric acid wastewater is generated.

Rhone Poulenc expected some weak acid wastewater when the regeneration unit started up in 1990, but the quantities were much larger than anticipated. The wastewater has to be neutralized on site before being sent to a publicly owned treatment works (POTW), and larger quantities meant added costs. For the business to be viable, the process needed to operate as close to equilibrium conditions as possible.

Plant personnel investigated the process throughout 1991 to determine what was causing the excessive weak acid generation. The investigative team looked at half dozen furnace variables.

- Temperature. The furnace temperature was varied between 1,600 and 2,000 degrees Fahrenheit.
- Air flow patterns. Different air flow combinations were tried, since combustion air could be taken in through various ports on the furnace.
- Acid atomizer locations. There are also numerous ports through which the spent acid can be sprayed into the furnace, and different atomizer spraying arrangements were tried.

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As a result, Rhone-Poulenc was able to reduce the amount of waste acid going to the publicly-owned treatment works by 75 percent.

- Air flow rate through acid atomizers. The atomization air pressure was varied.
- Sulfur flow rate and various air configurations. Different sulfur and air combinations were tried.
- Different spent acid strengths. Spent acids of different strengths were burned to determine if acid strength had an effect on weak acid generation.

The team discovered that too much oxygen too early in the process was one of the primary causes of the problem. Instead of sulfur dioxide (SO_2) produced in the furnace, sulfur trioxide (SO_3) was created. This extra oxygen atom made the difference. When SO_3 came in contact with water, sulfuric acid was formed.

Armed with this knowledge, the team modified operating procedures to minimize excess oxygen to raise the burning temperature and to maintain the optimum air flow patterns in the furnace. As a result, Rhone-Poulenc was able to reduce the amount of waste acid going to the publicly-owned treatment works by 75 percent. Acid went to acid and waste was minimized.

In addition, the caustic soda used to neutralize the acidic wastewater was reduced from 3,000 tons to 640 tons, saving more than $500,000 in material cost.

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"CLEAN" CLEANING

POLLUTION Using organic solvent to clean a process vessel resulted in 40 tons of contaminated solvent to be incinerated.

PREVENTION A high-pressure water wash reduced waste generation by 98 percent... and downtime.

Pots and pans are the biggest problem when doing the dishes — food sticks during cooking, and a strong detergent or extra elbow grease is needed to clean them. So it is when making chemicals, particularly polymers, which can stick like glue to process vessels.

At its Chambers Works plant in Deepwater, New Jersey, DuPont produces a specialized polymer used in aerospace and automotive applications. The polymer is made in a pressurized reaction vessel which has an internal agitator and baffles to promote complete mixing of the ingredients. In the course of manufacture, some of the polymer sticks to all surfaces — the sides, the baffles and the agitator — and must be removed periodically. In addition, the vessel must be cleaned between production runs of different polymer types. On average, the vessel at Chambers Works was cleaned every two weeks.

For 30 years, the cleaning agent was a flammable organic solvent. It smelled — imagine a thousand gallons of oil based paint drying in a confined space. The solvent was pumped into the vessel, agitated, and drained through a bottom flange into 50 gallon drums for incineration. This was repeated several times, resulting in 5,000 pounds of waste per wash in fugitive emissions and in a dozen drums that were handled partially by hand. Special precautions were required because the fumes could explode. The wash cycle took 24 to 32 hours, and the solvent didn't remove all of the polymer, which could cause quality problems.

In the late 1980s, a dedicated waste minimization project was authorized to recover and recycle the solvent, and a still was purchased. Before it could be installed, an internal Quality Improvement Team was formed to look broadly

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Cleaning takes less than four hours, cutting total turn-around time by 90 percent and increasing manufacturing capacity by 8 percent.

at process improvement. The team was headed by Richard Ric Debski, a transplanted New Englander and graduate of the University of Massachusetts with a degree in chemical engineering. The team set several process improvement objectives — to minimize waste, to shorten cycle times, to improve quality, and to reduce inventories — and considered four alternatives for cleaning the vessel:

- Open the vessel and clean it manually. Although this would eliminate the solvent, it would be difficult — the bolts were tightened to a torque 75 times greater than automotive lug nuts, for example — costly and time-consuming, and not attain the other objectives.
- Use an anti-stick coating on the vessel. This would reduce cycle time and reduce but not eliminate solvent washes.
- Use the still to recycle and recover. Although this would minimize waste, it would achieve no other process improvement objectives. In addition, the original recycling project was based on using drums, and when this was deemed inconsistent with other objectives, the projected capital costs soared.
- Replace solvent wash with a high pressure water jet. Although this would achieve all the objectives, it presented technical and safety problems. These water jets are used to cut rock and steel, and operate at water pressures of 40,000 pounds per square inch (vs. 40 pounds for a household shower).

An economic analysis was made of the last two alternatives, with water jet cleaning a clear choice. Its capital costs were $125,000 vs. $500,000 for recycling. The net present value — the value over time expressed in today's after-tax dollars — was a positive $2.7 million for water jet cleaning and a negative $350,000 for recycling.

A group came together to address the technical problems. For safety, cleaning would have to be done remotely, and the water jet completely enclosed within the vessel. Entry points should be limited, preferably to the bottom flange, and a special nozzle would be needed to reach all surfaces — walls, baffles, and agitator.

Stonegate, Inc., experts in water jet engineering, designed a special water lance and nozzle for the cleaning, using swivel technology, and a dozen DuPonters — mostly chemical operators and maintenance people, with combined experience of 300 years in the industry — made the process work. The prototype nozzle was tested in April of 1991, and the first system installed in December of that year. A chain drive, operated remotely by an operator several feet away, moves a rotating lance up and down inside the vessel. Cleaning takes less than four hours, cutting total turn-around time by 90 percent, and increasing manufacturing capacity by 8 percent. The solvent is eliminated, reducing waste generation by 98 percent. Savings include the costs of the solvent, of incineration, and of yield loss.

The system was installed in a second vessel in 1992, and in other vessels and processes in DuPont since then. A joint study published in 1993 by DuPont and the Environmental Protection Agency concludes that "high pressure water cleaning now presents an environmentally sound alternative [to solvent washes]. Where water cannot be introduced into the equipment, dry ice can be used."

In both cases, waste is cut dramatically. For DuPont at Chambers Works, downtime was cut as well.

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"WHITER THAN WHITE" WITHOUT THE WASTE

POLLUTION Production of an intermediate chemical used to make optical brighteners generated significant quantities of three different types of solid waste.

PREVENTION New chemistry for three production steps eliminated two out of the three wastes and reduced the third by 70 percent.

The advertising claim "whiter than white" is ensconced in today's laundry room. To get clothes that way depends on optical brighteners in laundry detergents. Optical brighteners absorb ultraviolet light and make it visible to the ordinary eye. The result: whites are whiter and colors are more vibrant. Optical brighteners for use in laundry detergents and in paper and textiles are the primary products at Ciba-Geigy's Brightener Business Unit in McIntosh, Alabama.

An important intermediate chemical is DAS or diaminostilbene disulfonic acid. DAS is formed through three different chemical reactions that enhance the ability to absorb light. At one time, solid waste was produced in all three reactions.

- In the first sulfonation, sulfuric acid was generated at one and three-quarters pounds per pound of product. Disposal costs ran $150,000 annually.
- In the second reaction, oxidation, bleach was used as an oxidizer and catalyst and total organic carbon (TOC) was generated. This step was inefficient in addition to producing waste. The harsh bleach destroyed part of the product, resulting in only a 75 percent yield.
- In the third reaction, iron was used to further modify the chemical and ready it for additional processing — leaving iron sludge in its wake. For every pound of DAS produced, one and three-quarters pounds of iron sludge was generated. This quantity was large enough to create a disposal problem for the plant but not large enough to be of any use to an iron foundry nearby.

Ciba was able to produce a more competitive product with better yields and expanded plant capacity — and with less waste (and disposal costs) at every stage.

In 1987 the McIntosh plant set out to reduce the wastes through process changes and spent the next five years overhauling the process to achieve the waste minimization objectives. Researchers Wolfgang Peter and Jurgen Bevrich developed the new processes in the lab. An operations team composed of Jack Kennatt, Wes McConnell, Jerry Mann and Dave Marshall were responsible for installing the equipment and implementing the new processes in the field.

The old sulfonation process used 25 percent oleum — a chemical produced by dissolving sulphur trioxide in sulfuric acid — and required dilution and filtration steps. This created the large volume of acid that had to be neutralized in the plant's wastewater treatment system. In revamping the process, a continuous sulfonation loop was installed, 65 percent oleum replaced the lower concentration, and the purification step was eliminated. The changes increased the concentration of the reaction solution and, as a result, sulfuric acid was eliminated and capacity increased by 50 percent.

Next, the team focused its attention on the oxidation step. Using a different solvent allowed bleach to be replaced by an oxidation utilizing a catalyst. This reduced TOC waste by 70 percent. What's more, the production yield increased by 17 percent and capacity was increased as well.

In the last change, the hydrogenation (the addition of hydrogen) was substituted for iron reduction, producing water as a by-product instead of iron sludge. This step realized a 20 percent increase in capacity and a 20-percent return on investment.

Ciba-Geigy McIntosh's efforts show the impact that process changes can have on waste minimization. Ciba was able to produce a more competitive product with better yields and expanded plant capacity — and with less waste (and disposal costs) at every stage.

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CHEMICAL COUSINS

POLLUTION An unwanted byproduct, "atactic" polymer, was the largest hazardous waste stream at the Phillips Petroleum Company's Houston Chemical Complex.

PREVENTION A more active catalyst produced the desired plastic, "isotactic" polypropylene, and reduced total hazardous waste.

Plastics have had a dramatic impact on life in the 20th century. They have been integral to advances in automotive technology, construction, packaging, electronics and medical equipment and clothing. One of the reasons is their infinite variety. Different processes and different starting points can produce a myriad number of plastics that possess the unique strength, weight and other physical properties required for specific applications.

The polypropylene plant at Phillips Petroleum Company's Houston Chemical Complex produces isotactic polypropylene, rigid in consistency, that is used in consumer products such as packaging, bottles, carpet and woven fabrics. The chemical reaction to produce the plastic depends on a catalyst to jump start it. The old process utilized a relatively low activity catalyst which produced a certain percentage of atactic polymer — a weak like cousin to isotactic polypropylene that is chemically different and not desired in this case — and had to be separated and disposed of. Roughly five to eight million pounds of atactic polymer were generated annually. The stream was flammable and therefore considered hazardous and was incinerated in a waste heat recovery boiler.

Plant management and operations personnel wanted to reduce the volume of atactic polymer to minimize waste and to improve the efficiency of the process. To accomplish this, the company licensed a new high activity catalyst technology which significantly increased the yield of isotactic polypropylene. The new catalyst required some redesign of processes and equipment downstream, the most significant of which was an increase in the number of steps to prepare and introduce the catalyst to the process. All equipment changes related to the new catalyst technology were fully implemented by December of 1993.

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These reductions represent a 47-percent decrease in total hazardous waste generated at the Houston Chemical Complex, a statistic that stands out.

Results were dramatic. The higher activity catalyst eliminated the generation of atactic polymer and enabled plant personnel to shut down the waste heat recovery boiler. What's more, about 221,000 pounds of permitted pollutants from the boiler stack and other emissions points were eliminated. These reductions represent a 47 percent decrease in total hazardous waste generated at the Houston Chemical Complex, a statistic that stands out. The State of Texas has acknowledged Phillips' waste reduction efforts as part of the Clean Texas 2000 program.

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SAVINGS IN TANDEM

POLLUTION 346,000 pounds of waste toluene were generated annually.

PREVENTION A distillation process was added to purify the toluene so it could be recycled, reducing waste generation by 70 percent.

Occidental Chemical (OxyChem) manufactures a paint additive at its plant in Ashtabula, Ohio. Toluene is used as a solvent to cut in several ingredients during the manufacturing cycle. The toluene is later separated from the additive and eventually is disposed of as a hazardous waste.

Production personnel identified the toluene by-product as a potential candidate for waste reduction in 1991. In order to ensure end product quality, OxyChem partnered with its customer to reduce waste generation, toluene emissions and raw material usage, and to share the economic benefits to be gained from the waste reduction effort.

An implementation team was formed consisting of Fred Eckert, plant manager; Dave Hunt, production manager; and Rick Eckert, process engineer. They were joined by Larry Holodniak, a chemist and laboratory manager, and Joe Pingyi, production general foreman.

The team wanted to recycle the toluene but had to overcome a major obstacle. Prior recycling attempts in 1988 resulted in recovered toluene that was not pure enough to be reused in manufacturing. The challenge became focused on recovering high quality toluene of value to production.

A different approach was initiated. Instead of stripping off the toluene, as was done in the past, plant personnel used existing, idle equipment to distill the toluene from the additive. The distillation process effectively removed impurities from the toluene so that it could be recycled back into the manufacturing process.

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The project was successfully implemented by 1993. Waste toluene was reduced from 346,000 pounds in 1992 to 96,000 pounds in 1993. OxyChem expects further reductions in 1994 — to 5,000 pounds a year.

The fact that OxyChem worked in tandem with its customer was unique. Once the new process had tested out successfully in house — and a favorable economic analysis was issued — the customer tested the paint additive made with the recycled toluene. The final approval on the process was given after successful lab and production trial runs.

The project was successfully implemented by 1993. Waste toluene was reduced from 346,000 pounds in 1992 to 96,000 pounds in 1993. OxyChem expects further reductions in 1994 — to 5,000 pounds a year. The project cost less than $50,000 to implement and saves the company about $80,000 per year — which OxyChem passes on to its customer.

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PLUGGING LEAKS

POLLUTION More than five million pounds/year of aceton, used as a solvent to produce vinyl resins, were emitted to the air.

PREVENTION Equipment and process changes, combined with workforce training, reduced emissions by two million pounds in the first year.

Acetone is a common solvent found in such consumer staples as nail polish and nail polish remover. At Union Carbide's plant in Texas City, Texas, acetone is used to produce vinyl chloride copolymers that end up in a wide range of products, including paints and coatings, floor coverings, sealants and adhesives.

In 1990, acetone air emissions at the Texas City plant were more than 5.3 million pounds. This was three-quarters of all air emissions from the plant and almost one-third of the Chemical and Plastic Division's total air emissions — big numbers.

While acetone is not considered a significant health or environmental hazard, Union Carbide wanted to reduce its emissions reported under the Superfund Amendments Reauthorization Act (SARA). The company assigned three experienced employees to the task. Team Leader Harry Moore, staff process engineer in the production department, and a 38-year veteran of the company, consultant Merle Eisenhour, a former employee whose ties to Union Carbide date back to 1946, and Denny Corwin, corporate fellow who had been with the company since 1953. These veterans were joined by Ray Jouett, senior R&D engineer, who came on board in 1989. The team's goal: to reduce acetone emissions by one million pounds each year for three consecutive years.

The team found a way to reduce emissions by two million pounds in the first year — exceeding its goal — without major ongoing operating costs.

The first step was to determine the sources and quantify the amounts of acetone leaking from fugitive sources. This was no easy task, since it involved

Once the sources of acetone leaks were identified, the team tackled the leakage problems through a combination of equipment and process changes, coupled with workforce training.

examining the entire department — covering four city blocks and including hundreds of pieces of equipment. Emissions were measured using a process known as "bagging" in which a plastic bag or balloon is used to seal off a leaking piece of equipment containing the leak. The gases trapped in the bag were allowed to escape at the same rate they entered and directed through a flow meter to determine the amount of gases leaking out. Samples of the gases were analyzed using chromatographic analysis to determine their composition. This measurement approach allowed team members to calculate the pounds per year of acetone being emitted at each point of leakage.

The team was surprised by the findings in many cases and gained a better understanding of the production process. Large emissions were found in areas where none were expected, and vice versa. The company had been calculating reportable emissions based on the difference between the amount of acetone purchased and the amount that left the plant in other products or in waste streams. The team found that an additional 100,000 pounds of acetone were being consumed in the production process and more acetone was leaving the process in identified waste streams than previously thought.

Once the sources of acetone leaks were identified, the team tackled the leakage problems through a combination of equipment and process changes, coupled with workforce training. First, repairs were made to equipment. Many of the leaks were traced to older tank vent units; by replacing roughly 40 of these 20- to 40-year-old units with updated equipment that had tighter seals, the team substantially reduced emissions.

Next, piping and a compressor were installed to collect and recompress the leaking acetone so it could be recovered in higher pressure distillation equipment with refrigerated cooling. The process left a very small amount of residual acetone which was incinerated.

Workforce training was an important part of the waste reduction effort. Union Carbide credits the ongoing success of its pollution prevention efforts to a team approach in which each employee — from the plant manager to each operator on the production line — is taught to be suspicious of acetone odors and is encouraged to bring problems and make recommendations for solutions to other team members.

The net result of these steps was that acetone emissions were reduced by over two million pounds in 1991 — double the original goals. Emissions in 1992 were reduced by another 900,000 pounds.

The project had bottom line benefits for the company as well. By reducing emissions, the company needed significantly less acetone in 1991, saving Union Carbide over $200,000 for acetone and other solvents which often accompany acetone.

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APPENDIX 2

PETROLEUM POLLUTION PREVENTION CASE STUDIES

AMOCO/USEPA POLLUTION PREVENTION PROJECT

Executive Summary

December, 1991
(Revised, May, 1992)

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SUMMARY

1.1 Project Goals

In late 1989, Amoco Corporation (Amoco) and the United States Environmental Protection Agency (EPA) began a voluntary, joint project to study pollution prevention opportunities at an industrial facility. The Amoco/EPA workgroup (Workgroup), composed of EPA, Amoco, and Commonwealth of Virginia staff, agreed to use Amoco Oil Company's refinery at Yorktown, Virginia (the Refinery), to conduct a multi-media assessment of releases to the environment, then to develop and evaluate options to reduce these releases. The Workgroup identified five tasks for this study:

1. Inventory refinery releases to the environment to define their chemical type, quantity, source, and medium of release

2. Develop options to reduce selected releases identified.

3. Rank and prioritize the options using a variety of criteria and perspectives.

4. Identify and evaluate factors such as technical, legislative, regulatory, institutional, permitting, and economic, that impede or invite pollution prevention

5. Enhance participants' knowledge of refinery and regulatory systems.

Figure 3.1 shows a schematic diagram of the Refinery, potential release sources, and a number of pollution prevention options identified in this Project. Table 3.2 describes specific options to reduce releases. At the time this Project began, pollution prevention was a concept predicated on reducing or eliminating releases of materials into the environment rather than managing the releases later. The Workgroup adopted this general concept and agreed to consider all opportunities--source reduction, recycling, treatment, and environmentally sound disposal--as potential choices in pollution management. Since then, Congress, in the Pollution Prevention Act of 1990, and other organizations, have put greater emphasis on source reduction as the primary, if not the exclusive, means to accomplish pollution prevention.

A central goal of this Project was to identify criteria and develop a ranking system for prioritizing environmental management opportunities that recognized a variety of factors including release reduction, technical feasibility, cost, environmental impact, human health risk, and risk reduction potential. Due to the inherent uncertainties in risk assessments, the Project focused on <u>relative</u> changes in risk

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compared to current levels, rather than establishing absolute risk levels. Because of difficulties in quantifying changes in ecological impact from airborne emissions, changes in relative risk were based primarily on human health effects indicated by changes in exposure to benzene. The risk assessment did not include a quantitative analysis of VOCs due to limited information on their health effects.

This project focused on pollution and potential risks posed by normal operation of the Refinery and chronic exposure to its releases into the environment. Minimizing emergency and upset events is a top priority of Amoco's facility managers. Such events can have catastrophic results. However, they were not studied in this project because: (a) prevention and control of such events involves significantly different skills, technical resources, and analyses than controlling releases from day-to-day operations (AIChE, 1985), (b) the number, type, and frequency of incidents at Yorktown is very low, and (c) data regarding the type of release, and relevant meteorology during the release are not available for analysis. Appendix D describes potential emergency and upset events that might occur at a petroleum refinery and the general preventative measures used to minimize their severity and the likelihood of their occurrence.

1.2 Project Organization, Staffing and Budget

Project Content. The Pollution Prevention Project has many components. Each component defines and addresses an issue associated with pollution prevention and facility management choices These include pollutant source identification, sampling, exposure modeling, risk assessment, etc. Table 1.1 provides a complete list of the components in this Project The Project workplan outlined the purpose and content for most of these components (Amoco/EPA, 1990).

Exclusions/Limitations: A number of areas specifically excluded or limited in this Project are described in Appendix B. Some are listed below.

- Limited sampling time and data provided a "snapshot" of releases rather than measured annual values.
- Very few generally accepted methodologies exist for the sampling used to obtain a site-wide release inventory, particularly for measuring air emissions. Both EPA and Amoco concerns about specific sampling issues are highlighted in Appendix B and discussed in more detail in Air Quality Data, Volume II (Amoco/EPA, 1992 b).
- The Project considered available technologies rather than exploring innovative techniques for reducing releases.

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- Chemical changes of airborne pollutants were not evaluated.
- Data and analysis focused on the Yorktown Refinery. Site-specific features of this facility and its emissions may not apply to other refineries. Broader regional concerns were not evaluated.
- The forthcoming human health risk assessment focuses on potential cancer risks associated with benzene exposure outside the facility fenceline.

Peer Review: At the Workgroup's request, Resources for the Future organized a group of outside scientific and technical experts. This Peer Review Group provided evaluation and advice on the Project workplan, sampling, analytical results, and conclusions. Members of this group were paid a small honoraria for their participation and reimbursed for travel expenses to Washington by EPA. A report summarizing their comments is included as part of the documentation for this Project Appendix C lists all Project documentation.

Workgroup: Monthly Workgroup meetings provided Project oversight, a forum for presentations on different Project components, and an opportunity for informal discussion of differing viewpoints about environmental management. Although attendance varied, each meeting included representatives from various EPA offices, the Commonwealth of Virginia, and Amoco

Workshop: A special Workshop, held during March 24-27, 1991, in Williamsburg, Virginia, reviewed sampling data and identified reduction options and ranking criteria. More than 120 people from diverse backgrounds--EPA, Amoco, Virginia, academia and public interest groups--attended the Workshop. The Workshop sessions resulted in suggestions that further refined and directed Project activities (Amoco/EPA, 1991a).

Participants: More than 200 people, 35 organizations, and many disciplines have been involved in this Project. Table 1.2 lists the various participating organizations.

Cost. Total cost for this Project was approximately $2.3 million. Amoco Oil Company provided 70 percent of the funding and EPA the remainder.

1.3 Lessons and Results

1.3.1 Refinery Release Inventory

A. Existing estimates of environmental releases were not adequate for making a chemical-specific, multi-media, facility-wide assessment.

The Yorktown Refinery had good information about the quantity of material released to the York River from NPDES Permit monitoring requirements, and for solid wastes as a result of internal programs and participation in recent American Petroleum Institute surveys (API, 1991b). These releases, however, made up only 11 percent of the total releases from the facility Available data did not include adequate chemical-specific characterization of the water discharge or solid waste streams.

The Refinery (and other refineries as well) could not easily identify specific airborne hydrocarbon compounds released or the quantity released because·

(a) Refineries typically do not manufacture products with specific chemical compositions, and therefore do not routinely measure chemical compositions of their products or emissions. Rather, refinery products have specific properties such as octane, freeze point, and sulfur content Crude oil, the raw material used to make these products, contains thousands of distinct chemicals that are never fully separated during the manufacturing processes. Airborne releases from this kind of facility are similarly complex.

(b) Most hydrocarbons are released through a large number of widely distributed sources (valves, flanges, pump seals and tank vents). Even a small refinery may have more than 10,000 potentially different sources Direct measurement of each of these sources is not practical.

(c) The quantities released through any single source are extremely small--on the order of pounds per year--dilute and difficult to measure. In addition, some large sources that emit pollutants in the amount of tons per year are difficult to measure and quantify. Total hydrocarbons released from Yorktown Refinery from <u>all</u> sources were approximately 0.3 weight percent of the total crude oil processed. Therefore, they would not be detected through normal mass balances and materials accounting (NRC, 1990).

Thus, collecting detailed, chemical specific release information used to characterize the Refinery was expensive and time consuming. This Project developed a sampling and monitoring program that included about 1,000 samples (see Figure 2.2). Each sample was analyzed for 15-20 chemicals. The sampling program took about 12 months to complete at a cost of about $1 million. Even with this time and dollar commitment, only selected sources were sampled The final release inventory was assembled using a

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combination of sampling, measurements, dispersion modeling, and estimates based on emission factors.

Because this sampling program was a first of its kind effort, its scope was intentionally broad. Subsequent analysis showed that not all of the information obtained was necessary to identify significant sources and potential reduction options. For the Yorktown Refinery (and the petroleum refining industry overall), more general information, such as source specific VOC emissions, is adequate to identify many of the pollution prevention projects developed in this study. Total VOC emissions are a good indicator of overall emissions and can be used for tracking emissions reduction progress.

B. A substantial portion of pollution generated at this refinery is not released to the environment.

The release inventory process allowed a comparison of pollutant generation, on-site management and ultimate releases to the environment. The Refinery generates about 27,500 tons/year of pollutants. As a result of site hydrogeology, on-site wastewater treatment, and solid waste recycling practices, about 12,000 tons are recovered, treated or recycled and do not leave the Refinery site Of the remaining 15,500 tons about 90 percent are released to the air.

Figure 2.4 illustrates the transfers which take place between generation and ultimate release. Figure 2.5 characterizes pollutants released from the Refinery. This site-wide analysis of pollutant generation and release characteristics allowed the Workgroup to focus much of the remaining Project resources on the largest releases--airborne emissions.

Modeling studies indicated relatively little naturally occurring transfer of hydrocarbon emissions from air into other media (Cohen and Allen, 1991). Most hydrocarbons are not very water soluble, and so are not easily removed from the air by rainfall Section 2 0 includes a more detailed discussion of the potential for transfer to other media. Although the fate of criteria airborne pollutants (like NOX and SO2) was not studied in this Project, they are known to be scavenged by rainfall and can contribute to nitrogen loads and pH changes in lakes and soil (See Appendix B) Measurements and modeling results showed small transfers from some surface water ponds to groundwater. Groundwater also enters the wastewater treatment system through the underground sewers, resulting in a net groundwater inflow.

Transfers of pollutants between media do occur, particularly as a result of pollution management activities. Over 370 tons/year of hydrocarbons initially present in wastewater streams are volatilized into air from the water collection system. More than

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2,000 tons/year of biosolids are produced by treating wastewater in the Refinery's activated sludge system.

C. The TRI database does not adequately characterize releases from this Refinery.

Title III of SARA, Emergency Planning and Community Right-to-Know Act, created the Toxic Release Inventory (TRI) in 1986. Title III requires regulated facilities in SIC Code 20-39 to submit annual release data on more than 300 chemicals manufactured, produced or otherwise used in quantities exceeding certain threshold values Releases to all media must be reported The TRI is one way of focusing corporate attention on release reduction opportunities.

TRI reports are based on either emission estimates, direct measurements or a combination of both methods. Each facility is responsible for the accuracy of the data reported. Industrial facilities frequently file amendments to TRI reports to reflect improvements in the accuracy of the estimation and measurement techniques.

The TRI database has become the de facto national release inventory. The quality and utility of data reported can vary widely. At a plant that uses a single solvent to wash manufactured parts, and that purchases extra solvent every year to make up for evaporative losses, the quantity of solvent emissions is well known and tracked through monthly purchasing records A TRI report which included this solvent and plant should be quite accurate. However, at the Refinery, the TRI does not report total facility emissions because:

- The TRI is based on estimates rather than measurements. Estimating accuracy varies widely. During the measurement portion of this Project, several new sources were identified whose significance had been previously underestimated One source was identified which had been overestimated. Figure 2 7 summarizes the results of this analysis.

- The measurement phase of this Project revealed substantially higher TRI reportable emissions from the blowdown stacks than had been estimated previously On the other hand, measurements revealed that emissions from wastewater sources had been overestimated. Amoco has filed an amendment to its past TRI reports for Yorktown to reflect new data. Figure 2.7 compares the starting TRI data with results obtained from the Project.

- The TRI focuses on specific chemicals which account for only a portion of the total emissions In the Refinery's case, the TRI report covers only 9 percent of the total

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hydrocarbons released, and only 2.4 percent of the total releases to all media. Criteria pollutants--CO, NOX, SO2, and PM-10--are not reportable in the TRI.

- Some activities and emissions are excluded by EPA from record keeping requirements, such as emissions from barge loading. At this facility, barge loading operations account for about 20 percent of the total benzene emissions (See Figure 3 4).

Finally, TRI provides an approximate inventory of selected materials released to the environment. TRI data by itself does not allow for meaningful risk evaluation or comparisons on a facility basis, because it does not define the facility's relationship to nearby populations and ecosystems.

D. Site specific features determined during the facility-wide assessment, affect releases and release management options.

National programs, by design, address overall problems in specific media. But these programs seldom consider site-specific differences in developing standards. Other refineries, and indeed other industrial facilities, can use the general sampling approach developed here to obtain the facility-wide release inventory. However, each site will exhibit unique geophysical and process characteristics. Each assessment plan must include these site-specific characteristics in its design and focus. As an example, the Yorktown Refinery does not have a hydrofluoric acid (HF) alkylation unit and HF was not measured HF can pose a significant health risk if managed improperly, and may need to be tracked at facilities that use it.

Groundwater: As a result of a clay soil layer, unique hydrogeology, the placement of the underground drainage system relative to the water table, and local climate, groundwater movement at this site is minimal. In fact, the underground drainage system is acting as a groundwater collection unit, sending groundwater to the Refinery's wastewater treatment plant. Thus, groundwater at this site is not leaving the property Furthermore, sampling showed surprisingly low levels of groundwater contamination, compared to other refineries (LA Times, 1988).

Marine Loading Emissions Yorktown Refinery uses marine transportation for receiving all crude oil and shipping more than 80 percent of its products. Estimated releases from product loading operations are 784 tons/year of VOCs. Computer modeling analysis showed this source had the greatest impact on exposure of nearby residences to Refinery hydrocarbon emissions Therefore, it would be useful to include marine loading emissions in this facility's environmental management plans. Many other refineries rely more on pipeline, rail and truck shipments to

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handle crude and products, and would thus not expect to find the same potential impact from marine operations.

Airshed Status: As discussed in Appendix A, the Refinery is located in an airshed classified as an attainment area for all criteria pollutants including ozone. Therefore, relatively few hydrocarbon emission controls have been required or installed at this facility. The sampling program and release reduction options focused on hydrocarbon releases. Many other refineries in ozone non-attainment areas have already installed extensive hydrocarbon emission controls. Consequently, other facilities may have a significantly lower percentage of hydrocarbon emissions Similarly, NOX, CO, PM-10 and SO2 emissions have been more tightly controlled in some other airsheds (such as the Los Angeles basin) which do not meet NAAQS for these pollutants.

1.3.2 Release Reduction Options

A. A workshop approach, drawing on a diverse group representing government, industry, academic, environmental and public interests developed a wide range of release reduction options in a multi-media context more quickly than EPA or industry alone would do.

The release inventory described in 1.3.1 above, served as the basis for identifying ways to reduce releases. A 3-day brainstorming Workshop, held in Williamsburg, Virginia generated more than 50 potential release reduction options for the Refinery. These ranged from producing a single grade of gasoline to specific technical options for particular equipment or processes Table 3.1 lists all options identified.

The Workgroup subsequently narrowed this list to 12 options for more careful, quantitative analysis. This winnowing process considered only those options that were technically feasible now, offered potentially large release reductions, addressed different environmental media, and posed no process or worker safety problems. Projects designed to comply with several current or anticipated regulations were also included. Table 3.2 lists engineering projects included for further analysis

The Workshop also addressed screening criteria to help prioritize the options, potential barriers and incentives for implementation, and permitting concerns. The diverse viewpoints brought to all these discussions helped guide subsequent Project activities These views reinforced the Workgroup's desire to consider broader issues such as multi-media release management consequences, future liability impacts, etc. The Workshop was able to consider these issues more comprehensively than either government or industry alone would normally do.

B. Release management frequently involves the transfer or conversion of pollutants from one form or medium to another.

It is not at all unusual for pollutants to be converted and transferred from one form or media to another as part of a pollution control practice. For example, scrubbers used to remove acidic pollutants from many electric utility stacks generate large volumes of calcium sulfate sludge (EPRI, 1983) which must also be managed. For options developed at the Yorktown Refinery

- Modifications of the underground drainage system and process water treatment plant (required under the Benzene Waste Operations NESHAP; Federal Register, 1990) will improve process water treatment and reduce air emissions, but produce more solid waste such as biosolids and fully spent activated carbon

- The Refinery has limited sludge processing capacity. Keeping soils out of sewers would reduce the amount of sludge in the API Separator and thus allow for more on-site management of other solid wastes, reducing offsite disposal.

- Installing an electrostatic precipitator would reduce FCU particulate (PM-10) emissions (catalyst fines), but transfer the additional collected particulates to land disposal.

- Burning hydrocarbons that cannot be economically recovered generates other criteria pollutants which may also need to be managed

None of these transfers or transformations are bad, in and of themselves. The Project simply pointed out the need to recognize, plan, and manage these changes at an early stage of the release management cycle.

C. Source reduction options were more cost-effective than most treatment and disposal alternatives. Nevertheless, source reduction alone was not adequate to achieve all the desired or legally required release reductions.

The Workgroup agreed to consider the waste management hierarchy--source reduction, recycling, treatment, and safe disposal--as the basis for developing release reduction options Technologies identified and analyzed fit into this hierarchy. Time and budget constraints limited technology choices to conventional, proven solutions rather than exploring innovative alternatives.

However, less than half the options identified qualified as "source reduction." Had the options been limited to only source reduction, the scope of potential opportunities for reducing

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releases and improving environmental quality would have been unnecessarily restricted.

If all source reduction options identified in this Project were implemented, benzene and total hydrocarbon emissions would be reduced by about 25 percent and 16 percent, respectively. The Workgroup concluded that a cost-effective strategy for the Refinery would have to include a mix of source reduction, recycling, treatment and disposal options

Of the source reduction options considered, most appear to be significantly lower cost than recycling, treatment, and disposal Source reduction options considered have had an average cost of $650/ton of pollutant recovered. The remaining seven options analyzed had an average cost of $3,200/ton, nearly 5 times higher The cost-effectiveness of individual options varied form a low of $190/ton for secondary seals on gasoline storage tanks to a high of $128,000/ton for the treatment plant upgrade.

D. While release reductions do not always pay for themselves, some environmental improvements can be made at a net cost savings to the Refinery.

The Refinery is relatively efficient in managing materials. An ongoing weight-loss management program to capture lost material has been in place at all Amoco refineries for a number of years Approximately 99 7 percent of the incoming crude is converted to useful products and refinery fuel The hydrocarbon release reduction options identified in this Project dealt with the remaining 0 3 percent.

Despite the relative efficiency of the Refinery, two source reduction options--seals on gasoline tanks and a leak detection and repair program--have net cost savings and a positive rate of return Amoco did not know this before this Project. On the other hand, some of the source reduction options and all treatment options were not economic investments for the Refinery For example, fitting all fixed roof storage tanks with secondary seals would result in much higher cost for relatively little additional reduction in hydrocarbon emissions compared to fitting only gasoline storage tanks. Treatment options generally require significant capital outlays with no return in the form of recaptured or improved product. Technology options with positive rates of return are shown in Figure 3.9. Options that have negative return are not shown.

1.3.3 Choosing Alternatives

A. Ranking the options showed that better environmental results can be obtained more cost-effectively.

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Compliance with current and anticipated regulations requires controls for eight sources types, reducing airborne hydrocarbon releases by 7,300 tons/year at an average cost of $2,400/ton. The Refinery could reduce about 7,100 tons of airborne hydrocarbons each year (or about 97 percent) by controlling six sources at about 25 percent of the cost. This cost-effectiveness comparison does not account for possible benefits to other media.

If allowed to address both hydrocarbons and listed hazardous waste, the Refinery could reduce about 7,500 tons per year at an average cost of about $500/ton using its choice of sources and techniques. Table 1.3 provides a more detailed comparison of different Release Management Strategies, results and costs

These results are all the more significant because the options evaluated were neither selected nor developed ahead of time with a target reduction goal in mind Nor did the selection process have a goal of meeting regulatory requirements in some alternative fashion. This suggests that even more impressive results might be achieved, if that were the focal point at the beginning.

B. All participants agreed on which options were the most effective and which were least, regardless of their ranking criteria or institutional viewpoints.

The Project used a multi-dimensional prioritizing process (the Analytical Hierarchy Process, AHP) in which weights were developed for all criteria used to rank alternatives. These criteria included cost, release reduction, timeliness and changes in benzene exposure, among others. The process allowed the Workgroup to assess the significance of and interactions between criteria--how changes in one criterion affect other criteria and total rankings

All options were considered legally acceptable, and no specific regulatory requirements were imposed on the decision making process. Although different organizations brought different perspectives to the discussions, each organization reached the same conclusions about which options would be most effective and which were least. The driving forces in this prioritization were cost and relative risk reduction, as measured by benzene exposure. A variety of sensitivity studies confirmed this initial set of preferences.

Amoco ranked control of marine loading losses as the most effective--though not the lowest cost--option. A second tier of options included installing secondary seals on tanks, instituting a leak detection and repair program, and upgrading blowdown stacks All four were also viewed as reasonably effective pollution prevention projects. In total these four projects would prevent or capture almost 6,900 tons of releases annually

at a cost of about $510/ton. EPA and Virginia selected the same five options, in this hypothetical case with no specific regulatory requirements. See Items 4 and 5 in Table 1.3

1.3.4 Obstacles and Incentives to Implementing Pollution Prevention

After identifying several alternative environmental management options, it is reasonable to ask why these options are not being implemented. What can be done to encourage their use? The following discussion summarizes the general findings based on an assessment of potential obstacles and incentives for implementing five highly ranked options For more details, see Section 5.0

A. EPA does not have an explicit policy goal and may not have the statutory authority to simply set a release reduction "target" without prescribing how this target should or could be met. When the target involves releases in multiple media, current administrative procedures discourage a coordinated approach, including evaluating risks, costs and benefits of managing residual pollutants in different media.

Requirements under many statutes and regulations prescribe how release reductions should be achieved, sometimes in terms of which technology should be used, often in terms of which specific sources should be controlled. For example, the Benzene Waste Operations NESHAP focuses on a specific emissions source to a single medium--benzene emissions from wastewater. The rule requires control of benzene emissions from this single source.

Data <u>from this refinery</u> indicated that wastewater is a small contributor to total benzene releases Amoco and EPA disagree about some of the specific measurements and results. These are discussed in detail in Air Quality Data, Volume II (Amoco/EPA 1992b)

A number of pollution prevention approaches developed in this Project are more effective in controlling benzene emissions, and less costly to implement than the benzene NESHAP. Other refineries might find other sources that present more cost-effective control opportunities. Focusing on individual sources, rather than on desired overall "performance," limits the ability to achieve the most cost-effective control

RCRA requires application of the Best Demonstrated Available Technology (BDAT) to a hazardous waste before it can be disposed. BDAT standards are typically based on a destruction technology rather than on methods at the higher end of the pollution prevention hierarchy.

One proposal now before Congress (S. 1081) to reauthorize the Clean Water Act would amend 304(b) of the Act and require EPA to

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promulgate effluent guidelines which reflect the application of best available control technology (BAT) for all categories of pollutants. This Congressional proposal, which does not reflect the Administration's position, could limit the Agency's ability to set environmental protection priorities.

B. Legislative and regulatory programs do not provide implementation schedules compatible with design, engineering, and construction timeframes.

Most regulatory and statutory programs require compliance within six months to at most three years after promulgation of a final rule. In some cases, compliance requirements do not consider normal maintenance schedules and economic penalties associated with facility-wide shutdowns. Consequently, short-term "fixes" which can meet legal deadlines, are used at the expense of more cost- and environmentally effective, long-term solutions.

A typical refinery project for processing oil using established technology and design procedures, normally takes 2-3 years from initial design to startup, assuming there is agreement on what to build, no unusual equipment delivery problems, no additional safety considerations, and no prolonged startup difficulties. Many projects take longer when regulatory applicability, scope or design criteria are unclear, or new technologies are involved

For example, the benzene NESHAP rule discussed above was promulgated in March 1990 (under the 1977 Clean Air Act Amendments). Statutory language required compliance with the regulations within two years. In this case, significant differences in interpretation between EPA and the regulated community took more than one year to resolve and to clarify the regulatory requirements. An acceptable understanding is a prerequisite to engineering and construction. It was physically impossible to design, engineer, procure, construct, and start up the required control within the remaining one year compliance time frame.

C. Congress, EPA and much of industry have become used to command-and-control, end-of-pipe treatment approaches based on twenty years of experience. These well established problem solving approaches are difficult to change.

In the 1970's, environmental regulations successfully helped reduce point source emissions to air and water. End of pipe treatment was successful partly because many industrial firms and permitting authorities had little experience dealing with these problems, and found the specification of technical solutions offered a "road-map" for how to proceed along an uncharted course. These requirements also provided a relatively "level playing field" for US industry. Many of today's problems are

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sufficiently different than those of the early 1970's that they can benefit from alternative approaches.

D. The short time taken by the Virginia Air Pollution Control Board to issue or modify air permits is not a deterrent to installing technologies to reduce airborne emission at this site.

Most of the technical options would reduce air releases at the Refinery. However, obtaining permits to install most of these technologies would probably not be a problem since the Virginia Air Pollution Control Board is estimated to take about six months to issue a permit (Virginia is a delegated state for issuing air permits).

However, information generated through a facility-wide multi-media assessment is a necessary first step to not only developing a strategy to reduce these releases, but also to exploring such implementation options as integrated permits.

E. Inadequate accounting for both the benefits and costs of environmental regulations is an obstacle to developing a more efficient environmental management system. Responsibility for pollutant generation and accountability for environmental protection are difficult to quantify.

At many industrial plants, such as Amoco's, waste management costs are frequently charged to a central environmental management division rather than to the operating unit that generates the waste. Remediation costs for clean-up of contaminated soil, for example, are frequently charged against another cost center, rather than to the generator of the contamination This separation between release generation and costs is a disincentive to manage releases more effectively

Few EPA accounting systems measure direct benefits of the Agency's activities, such as improved ecological health, biodiversity, reduced risk to human populations, etc. Rather, accomplishments are usually measured in terms of activities such as permits written, amount of fines collected, or number of enforcement actions pursued. (GAO, 1991) The lack of direct connection between Agency activities and environmental results reduces accountability for program costs and benefits. Without adequate measurement systems, it is difficult to tell when environmental management practices actually improve the environment.

1.3.5. Education/Communications/Working Relationships

This Project enhanced knowledge of both government and industry, and generated information that EPA and Amoco can use.

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The study provided an opportunity to educate individuals within EPA and Amoco. Based on plant visits and information exchanges, EPA personnel better understand how a refinery works, the complexities of the refining processes, and the difficulties in obtaining reliable environmental release data. This improved understanding will be useful as the Agency considers future data needs for regulatory development and permits.

Similarly, Amoco personnel better understand how EPA develops regulations, the type of information needed, and the Agency's operating constraints. This will be useful for Amoco in interacting with EPA and other government agencies.

The detailed release information developed in this Project could be useful to all three media offices: air, water, and solid waste.

- The Office of Air and Radiation may be able to use air monitoring and modeling information for developing MACT standards and improving emission factors
- The Office of Solid Waste should be able to use sampling and monitoring information for characterizing RCRA Subtitle D wastes and management practices.
- The Office of Water should be able to use wastewater sampling information to evaluate Petroleum Refining effluent guidelines, and the biomarkers research results in evaluating aquatic health measurement tools.

The working relationships between various EPA offices, State and Amoco personnel were quite fragile when the Project began Individuals brought their institutional viewpoints to initial discussions. By agreeing at the beginning of the Project that we may not necessarily agree with all findings and conclusions, people showed a willingness to discuss issues and focus on data and factual information Many of the perceived and real differences in views were more easily dealt with in a factual setting

1.4 Recommendations

1.4.1 Explore Opportunities to Produce Better Environmental Results More Cost-effectively.

Data from this study show that the Refinery can meet a release reduction goal more cost-effectively than by meeting reductions prescribed by current regulatory or legislative requirements.

For example, the ranking analysis shows that given the opportunity the Refinery could remove about 97 percent of tons of airborne hydrocarbons at about 25 percent of the cost of reducing

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them under current and anticipated regulations. The cost-effectiveness of the flexible option is about $600/ton compared with the cost-effectiveness of $2,400/ton for regulatory requirements.

EPA might evaluate options for setting a goal or target for reducing multi-media releases from a facility, and then allow the facility to develop an alternative compliance strategy to meet the goal. This alternative strategy would allow the facility to meet the goal at a lower cost, include interim milestones, and be enforceable. This strategy would also make appropriate information available to ensure that the reduction targets will be met.

This strategy might also include commitments to other environmental improvements such as cogeneration, additional reductions in releases, wetlands restoration, wildlife habitat enhancement, creation of new wetlands, controls on nonpoint sources of pollution, improved environmental data collection and research The cost savings realized from meeting requirements under a more flexible approach make it possible to realize additional environmental benefits which are presently foregone because of the high costs of many regulatory programs.

1.4.2 Improve Environmental Release Data Collection, Analysis and Management.

Data from this study show that an emissions inventory could be improved by measuring releases and developing new emission factors For example, the emissions inventory at the beginning of the project did not account for all potential releases to the environment. Some releases were excluded because the Agency has excluded them from reporting (e.g., barge loading operations); some releases were not included because the sources and the amount were thought by Amoco to be insignificant (e g , blowdown stacks), some emissions were overestimated (e.g., API Separator); and some releases were underestimated (e.g., coker pond) Jointly established sampling and analysis protocols could help improve data quality, so that reported values more accurately portray facility releases.

Data currently collected in response to regulatory or permitting requirements could be evaluated to determine how its utility and quality might be improved. For example, TRI data quality and utility could be improved by:

- Providing more inclusive estimates of facility-wide releases to all media. The Project found the exclusion of marine loading operations from TRI reporting requirements conveyed an inaccurate picture of total facility releases.

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- Reporting groups of chemicals, rather than individual species, especially if these chemicals have similar structural, physical and toxicological properties. Requiring reporting of all VOCs for refineries, rather than specific compounds like xylene (and its individual isomers), would provide a meaningful measure of refinery releases. That is because xylene poses approximately the same risks and has physical characteristics similar to the hundred of undifferentiated VOC compounds not covered in TRI. For a refinery, where a complex mixture of chemicals are released from most sources, tracking many separate chemicals does not make good use of technical, laboratory, and environmental management resources.

- Reporting other selected chemicals of concern for demonstrated human health or ecological impact separately. At a refinery, chemicals such as butadiene, benzene, and nickel may be good indicators of risk/release potential and management practices. Other industrial sectors would need to track different specific chemicals.

- Improving emission factors for estimating releases based upon information developed in this project, and additional work by EPA/industry task groups that could focus on the different data collection needs of discrete industry sectors.

The Project had great difficulty collecting and verifying environmental release data from the site Emissions from these sources are complex and measurement techniques are rudimentary. Many emission measurements varied with time For example, the Coker pond emissions varied by a factor of three within a few hours Better sampling and analysis methods and statistical tools are needed to analyze variability. Research is also needed to develop methods that can verify release inventories within reasonable confidence limits, accounting for specific differences in emissions factors.

1.4.3 <u>Provide Incentives for Conducting Facility-wide Assessments, and Developing multi-media Release Reduction Strategies. Such Strategies Should Consider Multi-Media Consequences of Environmental Management Decisions</u>.

This Project demonstrates that more cost-effective environmental protection programs can be designed by allowing companies to consider site specific factors and focus on results.

A detailed facility-wide, multi-media assessment identified the most significant medium (air) and releases sources, both in terms of quantity <u>and</u> impact on the surrounding area. Specific

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technology options were then developed to deal with these sources The significance of sources identified in this Project were not initially known or apparent to the participants Proposed solutions could not have been developed in the absence of data which identified their importance

For example, hydrocarbon emissions from barge loading operations (784 tons annually) and blowdown stacks (5,200 tons annually) are significant. However, the Refinery did not know this prior to this Project, nor did the existing regulations require the collection of this data. Thus, it did not develop control options to reduce these emissions.

Several technologies considered for reducing releases, transfer pollutants from one medium to another or convert pollutants to different forms. Since human health and environmental consequences vary from one medium to another, viewing a release problem in the context of net environmental effects is essential to developing more sound solutions.

The current institutional framework and procedures for developing regulations do not include multi-media assessments and analysis. Current practices should be reviewed to determine how they could be modified to use information from such assessments. An integrated pollution prevention and management strategy would facilitate development of release management options that produce better environmental results (EPA/SAB, 1990a; EPA/SAB, 1990b, OMB, 1991)

At present, industry has little incentive to conduct such assessments because it does not have an opportunity to implement their findings

1.4.4 Encourage Additional Public/Private Partnerships on Environmental Management

The Yorktown experience demonstrates the opportunities and pitfalls that can occur when government and industry work together The opportunities are significant. The pitfalls are worth overcoming. All organizations--EPA, Virginia and Amoco--sought to develop and test innovative environmental management approaches that, unlike most traditional "command and control" approaches, consider risk reduction, address multi-media concerns, maximize environmental benefits, encourage efficient use of resources, and promote facility-specific implementation choices. While it will take time and patience to overcome decades of distrust, such joint government/industry efforts can result in more cost-effective environmental protection by providing the opportunity to share different viewpoints and skills

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In this study, for example, EPA brought expertise on the type of information needed to develop regulations, and their operating constraints, while Amoco brought an understanding of refinery operations and economics. By helping to educate each other and develop a mutual understanding of issues and technology, Amoco, EPA and the Commonwealth of Virginia together agreed on the most significant emissions from the Refinery and the most promising approaches to reducing them.

Public/Private partnerships could also be used to leverage Agency resources for providing improved data needed to develop regulations. This Project illustrates a possible approach to collecting data, assessing technologies and characterizing a facility within an industry that took less time and Agency resources but relied more on private support.

1.4.5 Conduct Research on the Potential Health and Ecological Effects of VOCs.

The Refinery is a major source of the area's VOC emissions. However, information on the potential adverse health effects of VOC emissions is rather limited (Graham, 1991). Research is needed to better characterize health and ecological effects of VOCs that can be used in conducting risk assessments. This study could also build on efforts currently underway at the American Petroleum Institute, and the Chemical Industry Institute of Toxicology (CIIT) and others.

EPA should also undertake research to develop indicators that measure impacts on the ecosystem of multi-media releases from industrial facilities. This Project looked at several biomarkers that show promise as indicators in aquatic environments Limited information and methods for assessing ecological risk limits the ability to conduct comprehensive risk assessments, and measure changes in environmental quality.

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Table 3.2

Selected Pollution Prevention Engineering Projects

The following projects were identified for further study as a result of the Pollution Prevention Workshop in Williamsburg and subsequent Workshop meetings

1 Reroute Desalter Effluent. Hot desalter effluent water currently flows into the process water drainage system at Combination unit This project would install a new line and route this stream directly to the API Separator. This reduces volatile losses from the sewer system by reducing process sewer temperature and oil content. Volatile losses at the API Separator increase slightly.

2 Improve Desalter System: Evaluate installation of adjunct technology (e g , centrifuge, air flotation, or other technology) on desalter water stream prior to discharge into the underground process drainage system. This reduces oil and solids waste loads in the sewer system, affecting the waste water treatment plant and volatile losses from the drainage system.

3. Reduce FCU Catalyst Fines Evaluate possible performance of more attrition resistant FCU catalyst to reduce fines production (Subsequent review with catalyst vendors indicated the Refinery was already using the most attrition resistant catalyst available.) Two other fines reduction options were considered.

3a Replace FCU Cyclones Assess potential for reducing emissions of catalyst fines (PM10) by adding new cyclones in the regenerator.

3b. Install Electrostatic Precipitator at FCU· Assess potential of electrostatic precipitator in reducing catalyst fines (PM10) emissions.

4. Eliminate Coker Blowdown Pond: Change operating procedures for coke drum quench and cooldown so that an open pond is no longer needed This reduces volatile losses from the hot blowdown water.

5 Install Seals on Storage Tanks: Double seals or secondary seals will reduce fugitive vapor losses. Recovery efficiency varies from tank to tank, depending on the hydrocarbon stored and construction details. Table 3.3 provides additional information.

5a Secondary Seals on Gasoline Tanks: Secondary rim mounted seals on tanks containing gasoline.

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5b Secondary Seals on Gasoline and Distillate Tanks: Secondary rim mounted seals on tanks containing gasoline and distillate material.

5c. Secondary Seals on ALL Floating Roof Tanks. Secondary rim mounted seals on all floating roof tanks.

5d Option 5c + Internal Floaters on Fixed Roof Tanks· Secondary rim mounted seals on floating roof tanks and the installation of a floating roof with a primary seal on all fixed roof tanks

5e. Option 5d + Secondary Seals on Fixed Roof Tanks: Secondary rim mounted seal on all floating roof tanks and the installation of a floating roof with a primary and secondary seal on all fixed roof tanks.

6 Keep Soils out of Sewers: Use road sweeper to remove dirt from roadways and concrete areas which would otherwise blow or be washed into the drainage system. Develop and install new sewer boxes designed to reduce soil movement into sewer system, particularly from Tankfarm area. Estimate cost for installation on a Refinery wide basis. Both items reduce soil infiltration, in turn reducing hazardous solid waste generation.

7 The Benzene Waste Operations NESHAP requires control of benzene emissions from refinery wastewater sources. Three separate projects (7A, 7B, and 7C) were identified to meet these requirements Specific design and construction features of these projects will aid with meeting anticipated requirements of some future regulations, such as storm water permitting, RCRA corrective action, the Primary Sludge rule and land disposal restrictions.

7A Drainage System Upgrade: Install above-grade, pressurized sewers, segregating storm water and process water systems.

7B. Upgrade Process Water Treatment Plant: Replace the API Separator with a covered gravity separator and air floatation system Capture hydrocarbon vapors from both units

7C Convert Blowdown Stacks. Replace existing atmospheric blowdown stacks with flares. This reduces untreated hydrocarbon losses to the atmosphere, but creates criteria pollutants.

8 Change Sampling Systems. Install flow-through sampling stations (speed loops) where required on a refinery-wide basis These replace existing sampling stations and would reduce oil load in the sewer or drained to the deck.

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9 Reduce Barge Loading Emissions: Estimate cost to install a marine vapor loss control system. Consider both vapor recovery and destruction in a flare.

10 Sour Water System Improvements: Sour water is the most likely source of Refinery odor problems. Followup on projects previously identified by Linnhoff-March engineering to reduce sour water production, improve sour water stripping

11 Institute LDAR Program: Institute a leak detection and repair program for fugitive emissions from process equipment (valves, flanges, pump seals, etc) and consider costs and benefits

11a Annual LDAR Program with a 10,000 PPM hydrocarbon leak level

11b Quarterly LDAR Program with a 10,000 PPM hydrocarbon leak level

11c Quarterly LDAR Program with a 500 PPM hydrocarbon leak level

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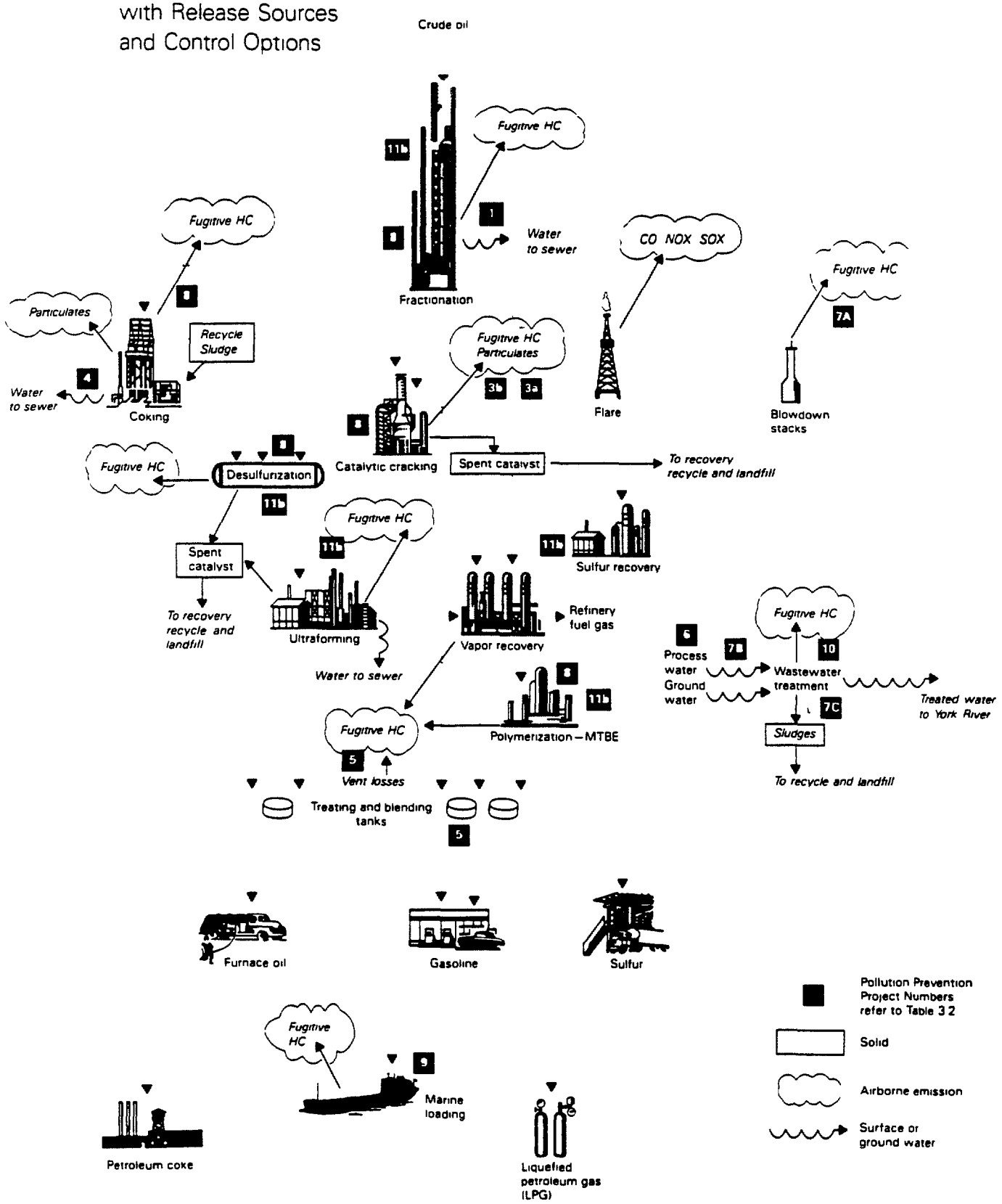
Figure 31

Yorktown refinery

Simplified Flow Diagram with Release Sources and Control Options



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Pollution Prevention in the

Chemical Industry

COURTESY OF THE CHEMICAL MENUFACTURER'S ASSOCIATION

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CATCHING WASTE AND CUTTING COSTS

POLLUTION *Eighty-three tons of a hazardous waste were generated during ethylene production.*

PREVENTION A new filtration system reduced the hazardous waste by 65 percent.

Occidental Chemical (OxyChem) uses nine heat exchangers to cool and remove impurities and particulates from the petrochemical gas stream at its Chocolate Bayou Plant in Houston, Texas. The plant makes ethylene and propylene from oil and natural gas.

Each month, two of the heat exchangers are removed for cleaning, generating a two-phase waste stream. Formerly, this waste was solidified with an absorbent prior to disposal. The resulting waste had a benzene content of 20 to 30 ppm and was classified as hazardous.

Plant personnel targeted this waste stream for reduction beginning in 1987. Ron Wages, environmental technician, organized a team that included Paul Davenport, waste disposal coordinator; Hymie Caul, waste disposal technician; Joe Moreno, maintenance engineer; and Harry Caul, operating technician, Olefins Unit.

The team determined that this hazardous waste would be substantially reduced by disposing of the liquids and solids individually, thus eliminating the use of an absorbent. Separation could be accomplished simply by using catch baskets with screens to filter the solids and collect the liquids.

The team initially considered installing a permanent stationary catch basket on each heat exchanger, but instead opted to design an innovative portable catch basket. The basket can easily be moved to any of the nine exchangers that are being cleaned. The total cost to implement the project was $5,500.

OxyChem's simple filtration system has had both environmental and economic benefits. Hazardous waste was reduced by 65 percent, or 108,000 pounds.

OxyChem's simple filtration system has had both environmental and economic benefits. Hazardous waste was reduced by ... 108,000 pounds per year. The company has saved $125,000 annually ...

year. The company has saved $125,000 annually in disposal and labor costs — adding absorbent to solidify the liquids was a labor intensive process.

This is the kind of project that enabled the Chocolate Bayou Plant to reduce hazardous waste generation by 58 percent from 1987 to 1993. The plant is a member of the Clean Texas 2000 Industry Honor Roll, which requires members to commit to reducing hazardous waste by 50 percent from the 1987 levels by the year 2000.

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Industry Experience With Pollution Prevention Programs

Pollution prevention is a multimedia concept that reduces or eliminates discharges to air, water, or land and includes the development of more environmentally acceptable products, changes in processes and practices, source reduction, beneficial use, and environmentally sound recycling

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Management support can help overcome a number of cultural and organizational barriers that can hinder a pollution prevention program The following are elements which historically have been used successfully to demonstrate management support to address such barriers

Support by management at all levels, made evident to the organization

- A clearly stated policy of top management support for pollution prevention including the expectation that all levels of management will seek appropriate pollution prevention opportunities in their operations
- An elevated internal appreciation of environmental issues in general and pollution prevention in particular, by including these issues in the assessment of goals and the performance of operating organizations
- An employee recognition program to promote and reward new and innovative ideas that lead to pollution prevention

Candor in dealing with internal and external perceptions and expectations regarding industry's environmental performance.

- Recognition that actions of the government and the public are guided by a belief that industry should do much more to protect and improve the environment
- Recognition that more environmental regulations and restrictions may be tempered by voluntary actions on the part of industry

Management Support

Recognition that concerns may arise over changing from the familiar approach of compliance with command-and-control requirements to an approach which emphasizes pollution prevention, however, this change can also offer opportunities.

- Acknowledgement that command and control requirements can provide certainty, but require specific performance which can also stifle creative and cost effective solutions Voluntary pollution prevention offers greater opportunity for flexibility creativity and optimization of solutions
- Recognition that a pollution prevention approach provides the greater opportunity to identify and exploit competitive advantages which may not be available under a command and control approach

Internal practices requiring that cost-effectiveness evaluations be performed for potential pollution prevention actions, including appropriate consideration of long-term benefits and otherwise historically hidden costs.

- Guidelines to assist in identifying and quantifying to the extent possible the long term benefits of potential pollution prevention actions, such as reduced liability, improved community relations, and improved employee attitudes, etc.
- Requirements to perform cost effectiveness evaluations which recognize long term benefits as well as short term costs and benefits including a full accounting of potential ' hidden costs (costs billed to other cost centers, etc.) for all pollution prevention activities

Operating Practices

A number of practices in operating organizations have been used to successfully identify evaluate, plan, and implement pollution prevention activities Building on management support, these practices form the nucleus of the program Specific practices which have been found to be effective include

Organizing to carry out the program

- Establishing a steering committee including knowledgeable representatives from operating functions and appropriate administrative areas, to develop and coor dinate the overall company program
- Establishing implementation teams or quality teams (or circles) in the operating organization to identify evaluate, plan, and guide the implementation of pollution prevention activities in their areas

Implementing the program in each operating function on a facility-specific basis.

- Developing an inventory of releases to all media Concentrate efforts initially on the most significant releases, including information about where and how each release originates any intermediate handling or processing, and its ultimate dis position
- Evaluating each inventoried waste stream and emission in order to develop plans for reductions Evaluation criteria might include quantity, toxicity, safety or health risk potential liability, level of public interest, technological feasibility and anticipated cost of reduction and availability of the resources necessary to accomplish the reduction Opportunities should be identified to move up the waste management hierarchy (from treatment and disposal to recycling or reuse to source reduction) when feasible and justified
- Setting realistic reduction goals both short term and long term (e g , one and five years), using the evaluations of inventoried releases to identify and prioritize the reduction steps which will attain the goals Combining the goals and the individual reduction steps can form an overall pollution prevention plan for the facility
- Accomplishing reductions including those identified in the plan and monitoring and reporting progress The plan should be flexible and therefore, should be updated periodically to reflect new information or changing situations

Communicating plans and results of facility pollution prevention programs.

- Establishing networks for sharing information among all company facilities about plans, successful (and unsuccessful) reduction techniques and progress
- Reporting to the company steering committee regularly for consolidation of plans and results for communication to management and others
- Providing feedback to employees on successful pollution prevention activities

Administrative, accounting, and communication practices can be established or modified to facilitate the adoption and implementation of a pollution prevention program Such practices can serve to reinforce management's commitment and to provide tools which support the program Actions which can be taken in these areas include

Establishing administrative processes to encourage the identification of pollution prevention opportunities.

- Instituting practices to identify and evaluate pollution prevention opportunities in research activities, designs for new or modified facilities, maintenance turnarounds, and reviews of proposed projects
- Broadening environmental compliance audit programs to include assessments of the extent to which pollution prevention opportunities are being identified, evaluated, and pursued when appropriate

Administrative, Accounting, & Communication Practices

Fully utilizing cost accounting and stewardship systems to support pollution prevention

- Within a plant's cost accounting system, fully identifying costs for controlling emissions and treating/disposing of wastes and allocating them to the operating units which generate the emissions and wastes
- Including accountability for the above costs, along with pollution prevention activities and progress in stewardship reports and reviews by all levels of management

Undertaking communication activities to increase pollution prevention awareness on the part of employees and others.

- Emphasizing the importance of pollution prevention in applicable training programs and in various forms of communications with employees
- Establishing employee incentive programs encouraging the generation of pollution prevention ideas

For more information consult the following

- STEP Strategies For Today s Environmental Partnership To change how our industry is perceived we must demonstrate that we are serious about protecting the environment American Petroleum Institute Publication Order No 877 69050 For copies call 202 682 8375
- API Recommended Practice 9000 Management Practices, Self Assessment Processes and Resource Materials American Petroleum Institute Publication Order No 878 90000 For copies call 202 682 8375
- Pollution Prevention Act of 1990 Enacted by Public Law 101 508 Nov 5 1990 104 Stat 1388 42 U S C 13101 et seq
- U S Environmental Protection Agency Facility Pollution Prevention Guide Office of Research and Development EPA/600/R 92/088 May 1992 For Copies Call 513 569 7562
- Total Quality Management A Framework For Pollution Prevention President s Commission on Environmental Quality January 1993 For copies call 202 395 5750
- Environmental Dividends Cutting More Chemical Wastes M H Dorfman W R Muir C G Miller INFORM Inc (1992) For copies call 212 689-4040

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The API Pollution Prevention Task Force has been actively involved in promoting pollution prevention within the industry since 1990 During that period the members of the Task Force have accumulated a comprehensive body of knowledge on the subject of pollution prevention along with an appreciation of many of the key elements that make pollution prevention programs successful The following resource document is a work product of the Task Force aimed at capturing their experience and knowledge and passing it along to API member companies It is intended only as a summary of elements that have proven to be successful for others

Benefit Overview

- Pollution prevention can be a cost effective means of reducing releases (air water and waste)
- Pollution prevention can reduce the cost of operating and maintaining existing release control equipment as well as costs associated with the rerunning of off test and slop materials
- Pollution prevention programs integrate well with new or existing "Quality Management Programs"
- A pollution prevention program can be an efficient means to consolidate and extend release reduction activities already underway
- Pollution prevention can provide a less costly alternative to the traditional government command and control approach
- Successful industry pollution prevention programs could act as models for such programs that may be developed by states and the federal government

Element Overview

Elements Historically Found in Successful Pollution Prevention Programs

Management commitment and support to help overcome cultural and organizational barriers

- Supportive policies, reinforced by actions
- Realistic handling of environmental performance perceptions and expectations
- Emphasis on potential benefits of pollution prevention vs traditional waste management methods
- Insistence on complete evaluations of cost effectiveness

Operating practices to identify evaluate plan and implement the program

- Organizational steps to carry out the program (establishing teams empowering team members setting aside resources etc)
- Procedures to implement the program on a facility specific basis
- Information sharing among affected parts of the company

Administrative accounting and communication practices to facilitate the program

- Processes to encourage identification of pollution prevention opportunities
- Cost accounting and stewardship systems
- Communication with employees and other interested parties