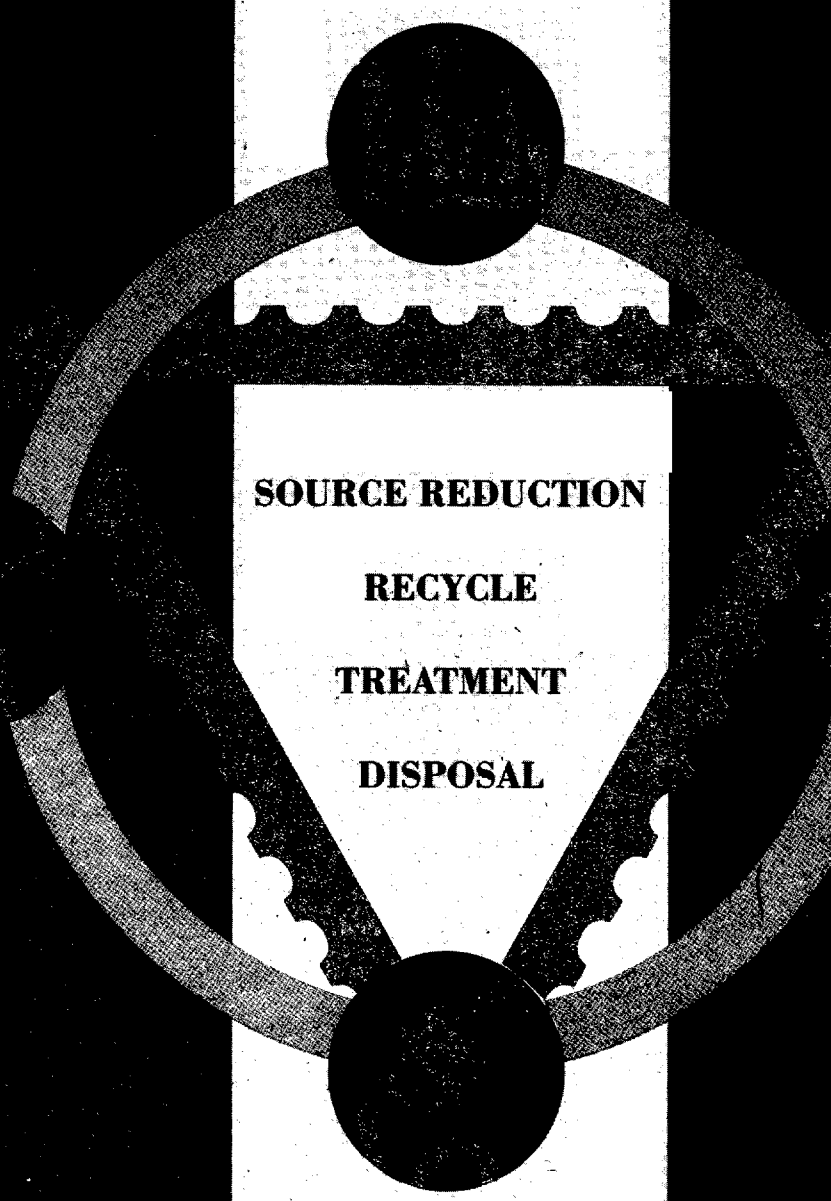


WASTE MINIMIZATION IN THE PETROLEUM INDUSTRY



SOURCE REDUCTION

RECYCLE

TREATMENT

DISPOSAL

A COMPENDIUM OF PRACTICES

Waste Minimization in the Petroleum Industry a Compendium of Practices

Health and Environmental Affairs

PUBLICATION NUMBER 3020

NOVEMBER 1991

**American
Petroleum
Institute**



Acknowledgements

This project was performed by the American Petroleum Institute (API) through the combined efforts of consultants, company representatives, and API staff. Mittelhauser Corporation, in conjunction with the API Waste Minimization Task Force, developed the concept and assembled the bulk of the document. R.G. Mattson brought additional marketing expertise to the project. Christina Griffin of Delta Analytical, Inc and Alan J. Senzel assisted in the technical edit of the report. Rick Stalzer of BP America, Don Hitchcock of Texaco, and Joel Robbins of Amoco made substantial contributions to the technical details. Barbara Bush of API's Health and Environmental Affairs Department served as Project Officer. The API Refining, Marketing, and Production Departments and Office of General Counsel provided essential review of the technical information which facilitated completion of the document.

.....

FOREWORD

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precautions, nor undertaking their obligations under local, state, or federal laws.

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

API makes no recommendations regarding the course of conduct that should be followed, and the reader is in no way bound to the findings of this study. The reader should exercise independent judgment that suits individual needs and must negotiate independently with the suppliers of any technology.

API makes no promises, claims, or recommendations as to the site specific applicability, performance, or economics of any technology described herein. The reader is cautioned regarding the interpretation of any references to "costs" or "cost effectiveness" as these references may not be applicable to his/her specific application.

This guideline may be used by anyone desiring to do so. Every effort has been made by the American Petroleum Institute to assure the accuracy and reliability of the material contained in it at the time in which it was written; however, the institute makes no representation, warranty, or guarantee in connection with the publication of this guideline and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any federal, state or municipal regulation with which this guideline may conflict, nor does the institute undertake any duty to ensure its continued accuracy.

Preface

The American Petroleum Institute (API) sponsored the preparation of this document, "Waste Minimization in the Petroleum Industry: A Compendium of Practices", which summarizes many practices currently used in the exploration and production, refining, and marketing segments of the oil industry. Thirty-five industry respondents were surveyed to provide information on practices to minimize waste volume or toxicity. Additional information has been developed from literature review of practices in the oil, chemical, and utility industries. The regulation of many of the streams and practices contained in this report has been changing rapidly. Therefore, careful review of all federal, state, and local laws and regulations should be undertaken before implementation of any of the practices contained herein. The Compendium is intended to provide a summary of current practices and is not intended as a basis for regulatory compliance.

Executive Summary

In early 1988, the American Petroleum Institute undertook a project to develop this document, "Waste Minimization in the Petroleum Industry: A Compendium of Practices" for the production, refining, and marketing segments of the industry. The following pages demonstrate the petroleum industry's keen awareness of the importance of minimizing waste, a worldwide trend that represents the wave of the future for all industrial processes.

This Compendium focuses primarily on widespread practices to reduce the volume and toxicity of solid and liquid wastes generated by a multitude of operations and maintenance activities within the oil industry. Increasing costs and potential liabilities for disposal of wastes are providing ever-increasing pressure to develop cost effective means to minimize the amount of waste generated by every industrial facility. Indeed, minimization of waste has become an integral element of all good industrial waste management programs.

Waste minimization practices can generally be divided into three categories. First, eliminating as much waste as possible at the source of generation is a primary factor in ameliorating waste management problems. Second, recycling waste can have considerable economic benefits; in some cases, waste containing oil can be recycled back to operating units for recovery and/or conversion into saleable products. Third, treatment of waste can reduce its volume or toxicity and thereby help avoid high disposal costs. Treatment processes frequently recover oil for recycling and product water for reuse or disposal with normal wastewater effluent.

This Compendium reviews and summarizes the current state of the art in minimizing waste and reducing toxicity at oil industry facilities. Schematic diagrams of important processes are provided, and specific case histories with cost-benefit analyses are described in detail.

Increasingly stringent federal, state, and municipal regulations have provided opportunities and economic incentives for the petroleum industry to implement significant waste reduction programs. Large facilities must furnish biennial reports on their progress to the U.S. Environmental Protection Agency. Land disposal restrictions on listed refinery wastes require facilities to treat these wastes using Best Demonstrated Available Technology (BDAT) before placement on the land. Newly promulgated regulations are resulting in even more waste streams being characterized as hazardous.

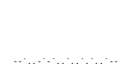
This Compendium is intended to help API members meet current and future challenges with regard to minimizing waste in the petroleum industry. Clearly, as the complexity and cost of hazardous waste management and disposal increase, waste minimization efforts will become top priorities for all facilities in our industry.

Table of Contents

Foreward	i
Preface	ii
Executive Summary	iii
Table of Contents	iv
List of Figures	viii
List of Case Studies	ix
1 Introduction and Document Use	1
1.1 Background	1
1.1.1 Questionnaire	1
1.1.2 Literature Survey	1
1.2 Using this Document	1
2 Waste Minimization	3
3 Exploration and Production Waste Minimization	5
3.1 Design and Planning Considerations	5
3.2 Drilling and Workover Fluids	6
3.2.1 Substitution of Drilling Fluid and Fluid Additives	7
3.2.2 Oil Separation and Removal from Drilling Fluids	7
3.2.3 Removal of Solids from Drilling Fluid	8
3.2.4 Segregation and Reuse of Drilling and Workover/Completion Fluids	8
3.3 Oily Sludges from Production Activities	9
3.4 Solvents and Chemicals	10
3.4.1 Amine Reclaiming	10
3.4.2 Triethylene Glycol Reclaiming	11
3.4.3 Saltwater-Contaminated DEA	11
3.4.4 Purge Streams from Sulfur Removal	12
3.4.4.1 Reclaiming/Recycling	13
3.4.4.2 Conversion to Chelated Iron Processing	13
3.5 Miscellaneous Used Materials	13
3.5.1 Empty Drums	13

	3.5.2 Used Oils	14
4	Refining Waste Minimization Practices	16
	4.1 Oily Sludges	16
	4.1.1 Control of Solids into Wastewater System	17
	4.1.1.1 Runoff Control	18
	4.1.1.2 Control of Exchanger Bundle Cleaning Solids	19
	4.1.1.3 Control of FCCU and Coke Fines	19
	4.1.1.4 Minimizing of Fine Solids Recycling	20
	4.1.2 Control of Surfactants in Wastewater System	22
	4.1.3 Desalter Brine Treating	24
	4.1.4 Filtration	25
	4.1.4.1 Belt Filter Press	25
	4.1.4.2 Recessed Chamber Pressure Filter (Plate Filter)	26
	4.1.4.3 Rotary Vacuum Filter	27
	4.1.5 Centrifugation	28
	4.1.5.1 Scroll Centrifuges	28
	4.1.5.2 Disc Centrifuge	29
	4.1.5.3 System Design	29
	4.1.6 Thermal Treatment	30
	4.1.7 Sludge Coking	31
	4.1.7.1 Quench Water Injection	31
	4.1.7.2 Coking Cycle Injection	32
	4.1.7.3 Blowdown Injection	32
	4.2 Tank Bottoms	32
	4.3 Fluid Catalytic Cracking Unit (FCCU) Decant Oil Sludge	34
	4.4 Purge Stream from Tail Gas Treating	35
	4.4.1 MDEA Conversion	35
	4.4.2 ADA and Vanadium Recovery Process	36
	4.5 Empty Drums	37
	4.6 Slop Oils	37
	4.7 Solvents	38
	4.8 Spent Caustics	39
	4.8.1 Recovery and Recycling of Phenols from Caustic	39
	4.8.1.1 Off-Site Recycling	40
	4.8.1.2 On-Site Recycling	40
	4.8.2 Recycling Sulfitic Caustic	40
	4.9 Spent Catalysts	41
	4.9.1 Recycling to Metals Reclamation	41
	4.9.2 Recycling to Cement	42

4.10	Spent Clay	42
4.11	Sandblast Media	42
4.11.1	Abrasive Blast Media	43
4.11.2	Copper Slag Abrasive with Recycling	43
4.11.3	Alumina Oxide Abrasive with Recycling	44
4.12	HF Sludge Media	44
4.12.1	Neutralization and Filtration	44
4.12.2	Production of Fluorspar	44
4.13	Cooling Tower Blowdown	45
4.13.1	Minimizing the Quantity of Cooling Tower Blowdown	45
4.13.2	Minimizing the Toxicity of Cooling Tower Blowdown	47
4.14	Miscellaneous Wastewater System Wastes	47
4.14.1	Replace Phenol Extraction	48
4.14.2	Changing Coagulation Chemical	48
4.14.3	Stormwater Diversion and Reuse	49
5	Marketing Waste Minimization	81
5.1	General Procedures for all Marketing Facilities	81
5.2	Classification of Marketing Segment Facilities	82
5.3	Refined Product Storage and Distribution Terminals and Bulk Plants	82
5.3.1	Terminal and Bulk Plant Yard Areas	82
5.3.1.1	Stormwater Runoff	83
5.3.1.2	Filter Separators	83
5.3.1.3	Air Eliminators	83
5.3.1.4	Loading Racks	84
5.3.1.5	Product Pump-off and/or Truck Unloading	84
5.3.1.6	Tank Car Unloading	85
5.3.1.7	Empty Drum Storage	85
5.3.2	Truck Maintenance Bays	85
5.3.2.1	Antifreeze (See also Section 5.5.5)	86
5.3.2.2	Solvents (See also Section 5.5.6)	86
5.3.2.3	Used Oil (See also Section 5.5.4)	86
5.3.2.4	Floor Cleaners (See also Section 5.4.2)	86
5.3.2.5	Truck Washing (See also Section 5.5.3)	87
5.3.2.6	Aluminum Brighteners	87
5.3.3	Tank Basins	88
5.3.3.1	Tank Water Draining	88
5.3.3.2	Sample House	89



5.3.3.3	Additive Injection Facilities	89
5.3.3.4	Tank Cleaning	90
5.3.4	Alcohols	91
5.3.5	Marine Docks	91
5.3.5.1	Dock Product Transfer Areas	91
5.3.5.2	Sanitary Waste	92
5.3.5.3	Ballast Water	92
5.3.5.4	Package Storage	92
5.4	Complex Marketing Terminals	93
5.4.1	Boiler Blowdown	95
5.4.2	Floor Cleaning	95
5.4.3	Used Oil	96
5.4.4	Loading Rack Slab Washing	96
5.4.5	Sludges from Separator and Sumps	96
5.4.6	Slop Oil and Commingled Product	97
5.4.7	Lube and Grease Manufacturing	97
5.4.8	Solvents (See also Sections 5.3.2.2 and 5.5.6)	98
5.4.9	Sampling and Laboratory Wastes	98
5.5	Retail Facilities (Service Stations, Fast Lubes, C-Stores and Truck Stops)	99
5.5.1	Underground Leaks and Product Spills	100
5.5.2	Underground Tank Water Bottoms	101
5.5.3	Car Wash (See also Section 5.3.2.5)	101
5.5.4	Used Oil (See also Section 5.3.2.3)	102
5.5.5	Antifreeze (See also Section 5.4.2.1)	102
5.5.6	Solvents (See also Sections 5.3.2.2 and 5.4.8)	102
5.5.7	Tires	103
5.5.8	Batteries	103
5.5.9	Oily Solid Waste (Filters, Sumps, Rags, Empty Containers and Absorbent)	103
	Bibliography	108
Appendix A	Questionnaire and Instructions	A-1
Appendix B	Letter of Transmittal for Production, Refining and Marketing	B-1

List of Figures

Figure 4.1-1:	Typical Refinery Solids Recycle Loop	50
Figure 4.1-2:	Integration of Sludge Treating Unit into Refinery Operation	51
Figure 4.1-3:	Desalter Brine Treating Unit	52
Figure 4.1-4:	Belt Filter Block Press Flow Diagram	53
Figure 4.1-5:	Plate Filter Press Block Flow Diagram	54
Figure 4.1-6:	Cross Section Diagram Recessed Plate Filter	55
Figure 4.1-7:	Rotary Vacuum Filter Block Flow	56
Figure 4.1-8:	Operation of a Horizontal Scroll Centrifuge	57
Figure 4.1-9:	Operation of a Disc Centrifuge	58
Figure 4.1-10:	Thermal Treatment Block Flow Diagram	59
Figure 4.1-11:	Process Flow Diagram Quench Water Injection	60
Figure 4.1-12:	Process Flow Diagram Coking Cycle Injection	61
Figure 4.1-13:	Process Flow Diagram Blowdown Injection	62
Figure 4.3-1:	FCCU Decant Oil Catalyst Removal System Block Flow Diagram	63
Figure 4.4-1:	Recovery Process Block Flow Diagram	64
Figure 4.8-1:	Phenol in Gasoline	65
Figure 4.8-2:	Phenolic Caustic Treatment	66
Figure 4.13-1:	A Simplified Schematic of a Cooling Tower	67
Figure C-4-4:	Deoiling of Desalter Effluent	74
Figure C-4-7:	Sludge Coking Process	78
Figure C-5-1:	Asphalt Waste Recycling	106

List of Case Studies

Case Study 3-1:	Filter Press	15
Case Study 4-1:	Street Sweeper to Reduce Oily Sludges	68
Case Study 4-2:	Reuse of FCC Fines	69
Case Study 4-3:	Alternative Sandblast Media and Recycle	70
Case Study 4-4:	Deoiling of Desalter Effluent	72
Case Study 4-5:	Screening of Solids from Exchanger Cleaning	75
Case Study 4-6:	Spent Jet Fuel Treater Clay Deoiling	76
Case Study 4-7:	Sludge Coking	77
Case Study 4-8:	Chemical Recovery Process	79
Case Study 5-1:	Asphalt Waste Recycling	104
Case Study 5-2:	Recycling of Soap Dust Waste	107



1 Introduction and Document Use

1.1 Background

Information from several sources was assembled to form this Compendium. A survey of API members was conducted using a questionnaire developed to gather practical information on actual practices. Additional information was obtained from literature sources such as technical papers from symposia and journals as well as various trade associations. A bibliography of these documents is presented just before the appendices. Those who worked on the preparation of the Compendium drew upon first-hand knowledge regarding waste minimization practices.

The Compendium was prepared to present the information in a form suitable for quick reference by top management and field personnel alike. The waste practices are presented according to the type of waste in question. In addition to descriptions of the practices, flow diagrams and case studies are shown where available.

1.1.1 Questionnaire

A questionnaire was distributed to a representative cross-section of API's members to develop information on minimization practices that are currently implemented in routine operations. This questionnaire covered information on facility size, waste quantity and characteristics, and descriptions of the waste minimization practices utilized. A copy of the questionnaire and the instructions for completing it are presented in Appendix A. Copies of transmittal letters sent to production, refining, or marketing facilities are attached in Appendix B.

1.1.2 Literature Survey

A literature survey was conducted to augment the information developed from the questionnaire. The literature search included reviewing published documents from a number of oil industry associations such as API, Western States Petroleum Association (formerly Western Oil and Gas Association), National Petroleum Refiners Association, Petroleum Association for Conservation of the Canadian Environment, and the U.S. Environmental Protection Agency. Additionally, literature from related industries and associations such as the Chemical Manufacturers Association was reviewed to determine those waste minimization practices that could potentially be applied in the oil industry.

1.2 Using this Document

The Compendium addresses practices and procedures for minimizing waste in the petroleum industry. It assumes that the reader has a basic understanding of relevant

regulations applying to the treatment and disposal of any waste generated and it does not attempt to discuss these in any detail.

The Compendium is divided into sections and subsections¹ as follows:

- Section 2: Waste Minimization. This section gives a general introduction to the concept of waste minimization. It describes background and the definitions of terms important in waste minimization: source reduction, recycling, treatment, and disposal.
- Section 3: Exploration and Production Waste Minimization.
- Section 4: Refining Waste Minimization Practices. (This section includes diagrams that illustrate how specific waste minimization measures operate or can be used.)
- Section 5: Marketing Waste Minimization.
- Bibliography: Provides the references that a reader can consult for further information.
- Appendix A: Questionnaires. (See description under background above.)
- Appendix B: Letters. (See description under background above.)

¹ NOTE: Sections 3, 4, and 5 are divided into numerous subsections describing techniques that can be used to reduce waste in specific activities within the sector. In addition, case studies and, where appropriate, diagrams are at the end of each section.

2 Waste Minimization

The concept of waste minimization became a more prominent part of waste management in 1984, when Congress reauthorized the Resource Conservation and Recovery Act (RCRA) with the Hazardous and Solid Waste Amendments (HSWA) and set forth the following policy with respect to the minimization of hazardous waste (Section 1003(b)):

The Congress hereby declares it to be the national policy of the United States that whenever feasible, the generation of hazardous waste is to be reduced or eliminated as expeditiously as possible. Waste that is nevertheless generated should be treated, stored, or disposed of so as to minimize the present and future threat to human health and the environment.

In its 1986 Report to Congress on the Minimization of Hazardous Waste, EPA clearly defined waste minimization to mean:

[T]he reduction, to the extent feasible, of hazardous waste that is generated or subsequently treated, stored, or disposed of. It includes any source reduction or recycling activity undertaken by a generator that results in either (1) the reduction of total volume or quantity of hazardous waste, or (2) the reduction of toxicity of hazardous waste, or both, so long as the reduction is consistent with the goal of minimizing present and future threats to human health and the environment.

Subsequent to the publication of the Report to Congress, EPA specially adopted and encouraged use of an integrated waste management hierarchy to solve solid waste generation and management problems. The hierarchy consists of a series of management options, namely source reduction, recycling, treatment, and disposal, that can be used to manage waste streams. The hierarchy concept implies that the management options are ranked in order of preference. The use of the term "integrated" implies that all of the management options work together to form a complete system for proper management of waste. API supports the use of an integrated waste management hierarchy because all of the "steps" embodied in the hierarchy are recognized as necessary to reduce the volume and toxicity of waste. While source reduction and recycling are clearly the preferred management options, the hierarchy allows for flexibility in selecting a mix of control technologies. The applicability of each of the management options in waste reduction will be dictated by the diversity of site-specific industrial and waste management operations as well as the feasibility and cost of the various options available.

Implementation of a waste minimization program usually follows the hierarchical sequence of source reduction, recycling, and treatment. Listed below are the preferred steps in the integrated waste management hierarchy and the generally accepted definitions of these steps as typically seen in the literature.

Source Reduction:

Source reduction refers to the reduction or elimination of waste generation at the source, usually within a process. Source reduction measures can include types of treatment processes, but they also include process modification, feedstock substitutions or improvements in feedstock purity, various housekeeping and management practices, increases in the efficiency of machinery, and even recycling within a process. Source reduction implies any action that reduces the amount of waste generated by a process.

Recycling:

Recycling refers to the use or reuse of a waste as an effective substitute for a commercial product, or as an ingredient or feedstock in an industrial process. It also refers to the reclamation of useful constituent fractions within a waste material or removal of contaminants from a waste to allow it to be reused. Recycling implies use, reuse, or reclamation of a waste either on-site or off-site after it is generated by a particular process.

Treatment:

Treatment refers to methods, techniques or processes that are designed to change the physical, chemical, or biological character of hazardous waste in order to render the waste non-hazardous or less hazardous. Treatment implies actions that render waste safer to transport, dispose, or store.

Disposal:

Disposal refers to the discharge, deposit, injection, dumping, spilling, leaking, or placing of any waste into or on land or water.

3 Exploration and Production Waste Minimization

The purpose of the exploration and production segment of the oil industry is to discover and deliver crude oil and gas to the earth's surface for transportation to refiners and users. The drilling of oil and gas wells and their subsequent long-term operation to produce crude oil are the main activities in this part of the oil industry.

The primary wastes generated during the drilling of oil and gas wells are drilling fluids and cuttings. The wastes generated by production of oil and gas are produced water and oily sludges. Secondary wastes such as used oil, drums, and chemicals are contributed from both drilling and production operations.

This section of the Compendium provides a description of fundamental concepts for waste minimization and some examples of specific practices where successful reduction of waste is being accomplished. Areas covered include the following:

- Design and planning considerations
- Drilling and workover fluids
- Oily sludges
- Solvents and chemicals
- Miscellaneous used materials

3.1 Design and Planning Considerations

The initial design of well sites and producing facilities often include review of waste generation and disposal practices. Planning and development of exploration and production wells, sites, and facilities can have significant impact on reducing the amount of waste generated. The design considerations and operating procedures discussed in the remainder of this subsection are examples of design approaches that will reduce waste.

The amount of waste generated during the drilling process is directly related to the size and the depth of the hole drilled. Generation of such waste will be minimized by keeping the hole drilled as near the diameter of the drill bit as possible. Drilling fluids that minimize reaction with the drilled formations and wellbore hydraulics that reduce borehole erosion are used to prevent enlargement of the hole.

The layout of the drilling site can significantly affect the amount of waste generated. Some drill sites are designed to divert rainwater and snow runoff away from reserve pits, thus reducing waste fluid volumes. Some locations that are environmentally sensitive or have a limited amount of land available use a single drill site to drill single or multiple wells directionally. Liquid/solids separation equipment is commonly used to remove drill cuttings from the drilling fluid. Use of vibrating screens, hydrocyclones, and centrifuges extends the usable life of the drilling fluid.

The volume of the fluid stream (oil, water and gas) received by production facilities is dependent upon reservoir pressure mechanisms, the method by which the well is completed, and the production rate of the well. These factors also have an impact on the waste components of the fluid stream, such as silt, sand, and water. Gravel packing and screens can reduce the amount of silt and sand solids produced by a well.

Generally, the design and rate of injection on enhanced oil recovery (EOR) projects can significantly improve the oil/water/solids ratio. The generation of waste solids will be limited by ensuring that water used for water floods is chemically compatible with the formation waters and formation layers. Chemical balancing of the injection water with the formation water can limit the formation of precipitates such as barium, calcium, and magnesium sulfates and calcium carbonates, thus reducing the degree of clay shrinkage that eventually causes fine solids to be carried along with the produced fluids. In steam floods, agents can be added to the steam and water prior to injection to promote separation of oil from the formation fines.

3.2 Drilling and Workover Fluids

Drilling and workover/completion fluids comprise the largest category of wastes generated during the development of oil and gas wells. Drilling fluids must remove cuttings, keep the hole stable, and contain formation pressures without damaging the producing capacity of the reservoir. The cost of making up these fluids and disposing of them are driving forces for reducing the amount of drilling fluid needed, and for recycling and reusing drilling fluids whenever possible.

Drilling fluids are disposed either because of excess volumes from casing and cementing operations or because of contamination from drilled formation solids or fluids. The required volume of drilling fluid will change during the drilling operation. For example, when casing is run and cemented in a newly drilled hole, the required drilling fluid volume is reduced and the displaced fluid becomes surplus. Also, during drilling, different geologic zones are encountered which usually require alteration of drilling fluids and/or their chemical/physical properties. Drilling fluids are often completely replaced at critical geological junctions or are altered with additives in response to dynamic hole conditions. Complete drilling fluid replacement will generate large volumes of excess fluid which may be stored for future use or, more typically, disposed.

Contamination can also result in the need to dispose of some or all of the existing volume of drilling fluid. Common contaminants are dissoluble formation salts such as gypsum, sodium and potassium chloride, and anhydrite. Occasionally, the concentration of drill cutting solids in the drilling fluid will rise to the point that treatment or disposal of the fluid is necessary before drilling can resume. Other activities, such as cementing wells or drilling out cement plugs, can cause contamination of the drilling fluid and render it unusable.

Alternative operating procedures used in the industry to minimize the volume or toxicity of waste drilling fluids are described in the following subsections.

3.2.1 Substitution of Drilling Fluid and Fluid Additives

In response to environmental and regulatory trends, the drilling fluid industry has tested many fluids and has verified that a large number are not toxic at recommended use concentrations. In addition, the industry has developed several alternative drilling fluid systems that minimize the impact on the environment. Alternative drilling fluids and additives include:

- Chrome-free lignosulfonates and polysaccharide polymers to replace chrome lignosulfonates for reducing drilling fluid viscosity.
- Effective lubricants such as lubra beads and gilsonite-based additives to replace diesel oil.
- Isothiazoline and amines to replace pentachlorophenols and paraformaldehyde as biocides.
- Mineral oil in place of diesel oil as an effective substitute for stuck pipe spotting fluids.
- Low solids nondispersed drilling fluid systems to replace dispersed systems which typically require large volumes of water.
- Sulfite and organic phosphate corrosion inhibitors to replace chromate corrosion inhibitors.

3.2.2 Oil Separation and Removal from Drilling Fluids

In water-based drilling fluids, the oil component of the circulating fluid is usually quite low, less than five percent by volume. Oil can enter the circulation fluid system from drill cuttings, from oil reservoir fluids which enter the well bore when fluid hydrostatic pressure is less than reservoir pressure, or from occasional addition of oil to the drilling fluid system to achieve higher lubricity.

Oil that has been added as a pill (a small, 20 to 50 barrel slug) can often be separated by diverting the annulus stream into separate tanks at the time it returns to the surface. Oil that has entered the system from the well bore is not as easily removed. Some oil will be emulsified in the drilling fluid where it does not normally create a disposal problem.

Oil that rises to the surface of the drilling fluid reserve pit can cause disposal and treatment difficulties. This oil is removed by skimming it off with vacuum trucks or by

using oil skimming devices. The reclaimed oil can be recycled to the production process for eventual sale.

3.2.3 Removal of Solids from Drilling Fluid

The primary function of solids control equipment is to separate drilled formation solids/cuttings from drilling fluid. Principal pieces of equipment used to remove formation solids from fluids include the following:

- Shale shakers
- Desanders
- Desilters
- Mud cleaners
- Centrifuges

Most of these solids control devices provide relatively dry solids for disposal. Solids are on the order of 30 percent water by weight. Optimal use of liquid/solids separation equipment greatly reduces waste fluid volumes and maximizes the useful life of drilling and workover/completion fluids.

Drilling fluid dilution, as a result of poor solids control, leads to increased fluid volume and will increase the amount of fluid that must eventually be discarded. In some cases, there may not be an alternative to diluting a drilling fluid. Usually, however, chemicals are used in conjunction with the solids control equipment to eliminate the need for dilution water that adds to waste volume.

With advances in solids control equipment and chemical additives and the use of additional storage tanks, some drill sites have instituted a closed loop system in which drilling fluid is processed by a sophisticated application of solids removal equipment. The equipment can include a centrifuge/polymer flocculation process which completely separates the drilling fluid into liquid and solid components. The liquid component is reused for the makeup of new drilling fluid or for washdown operations on the drilling rig. This process can reduce the volumes of waste that are generated under drilling. However, it is not feasible in many situations.

3.2.4 Segregation and Reuse of Drilling and Workover/Completion Fluids

The segregation and reuse of drilling and workover/completion fluids has been a long-standing practice in the oil and gas industry. The trend is growing with the industry's continuing effort to reduce waste and the cost of disposal.

Many circulating fluids can be segregated into components and reused. Restoration and reuse of the fluids may be accomplished either on-site or off-site.

On-site restoration and reuse is usually limited to water-based drilling fluids and workover/completion fluids. On-site restoration relies primarily on solids control equipment which is normally provided by a contractor. Specialized equipment may be brought to the site for further refinements. Sock filters or centrifuges and/or filter presses are particularly beneficial for removing solids from completion and workover fluids, which are often required to be nearly solids-free. On-site restoration is common on offshore platforms because the drilling fluid can often be used on the next well to be drilled. Similarly, the drilling fluids from the intermediate and production section of the borehole can be segregated, restored, and reused on other wells.

Sometimes drilling fluid is processed and used strictly for its water content. Separated water can be used to make up new drilling fluids or be used as rig wash water.

Barite is another component that can be reused in the drilling fluid system. Centrifuges are often used to recover barite from barite-weighted drilling fluids both to prolong fluid usefulness and for fluids that are destined for disposal.

Most drilling rigs are not equipped to restore oil-based circulating fluids completely or to store them for future use. Oil-based drilling fluids have a high oil content, are costly, and are typically returned to the original vendor. Vendors repurchase oil-based fluids from the operator with price reductions applied for entrained water and/or solids. In specialized plants, vendors remove the solids and prepare the oil-based fluid for resale.

3.3 Oily Sludges from Production Activities

Oily sludges will be generated any time production fluids are slowed sufficiently to allow produced sediments and/or water to settle. Fine solids that have entered the well bore, along with hydrocarbons and water, form a relatively stable colloid sludge as they are reduced and mixed through the production string and the surface handling system. Water and water/oil emulsions which have coated the fines tend to settle to the bottom of temporary storage tanks or separation devices. Once the sludges have formed they are not readily handled by most on-site production facilities. Examples of oily sludges include:

- Tank bottoms and emulsion layers
- Heater treater sludge
- Flotation wastes
- Pigging wastes
- Water handling sludge

Production facilities employ various procedures to prevent, reduce, or recycle these oily sludges. For example, certain biphenyl-based chemical emulsifiers can be injected downhole to combine with the produced oil and water. When the produced fluid is brought to the surface, the crude oil more readily separates from the produced water

without forming emulsified sludges. In certain locations, third-party recyclers will take oily sludges for a reasonable fee and recover the oil content for recycling. These recyclers use centrifuges, heat, or filters to separate the oil, solids, and water. Other service contractors are available to set up at the production field and use transportable treatment units to remove oil and water from sludges and reduce the volume of disposable wastes.

Service contractors generally provide centrifuges or pressure filters to recover oil and water from the oily sludges described above. Producers usually provide portable or permanent tankage to accumulate the various oily sludges over a reasonable time. Because service contractors charge a fixed fee for setting up their equipment, it is usually cost-effective to accumulate a large volume of oily sludge before calling in a service contractor.

Various technologies available to separate oil and water from sludges are discussed in more detail in Sections 4.1.4 through 4.1.6 of this Compendium.

3.4 Solvents and Chemicals

Many of the large scale oil and gas production fields include substantial processing facilities to remove oil or gas impurities before pipeline transfer. These processes invariably employ chemicals and solvents that eventually require disposal. Procedures for handling these wastes are described below.

3.4.1 Amine Reclaiming

Various amine-based aqueous solutions are used in treating gas to remove hydrogen sulfide and carbon dioxide (acid gases). Examples include monoethanolamine (MEA), diethanolamine (DEA), and methyl-diethanolamine (MDEA) solutions. The solutions become contaminated with production field contaminants, corrosion products, reaction by-products and solvent degradation by-products. Continued use of the degraded solution results in operating problems and performance loss. Consequently, the solution must be regenerated, reclaimed, or disposed.

With the exception of MEA, reclamation of the solution has generally been considered impractical. DEA, for example, will degrade at the temperatures required to distill it at atmospheric pressure. As a consequence, these amine solutions are withdrawn from service and disposed as a chemical waste, usually through an injection well.

In some cases a CO₂ absorption reclaimer may be able to effectively reclaim high molecular weight amines such as DEA, MDEA, and diisopropylamine (DIPA). Hot CO₂ has the capacity to evaporate and absorb alkaline treating solvents and carry solvent vapor to a cooler where vapors are condensed back to a liquid and recovered. The evaporation can be accomplished at a temperature below the amine's degradation temperature.

The process uses a kettle-type heat exchanger with an oversize steam tube bundle designed to use 65 psig steam which maintains a kettle liquid temperature of about 280 degrees F. The CO₂ is preheated by overhead heat exchange. In the kettle, CO₂ absorbs solvent from the liquid surface. Solids in the amine solution are left to accumulate in the kettle. Saturated CO₂ containing solvent and water exits the kettle overhead and passes through heat exchange; solvent and water are then condensed.

3.4.2 Triethylene Glycol Reclaiming

Triethylene glycol (TEG) is used as a dehydrating agent to remove water. Following its use in field wellhead dehydrators, it is also used downstream following acid gas removal. TEG in wellhead dehydrators accumulates salt and should be replaced before the salt concentration reaches 5,000 ppm. TEG in gas plant dehydrators picks up solvent carried over from the acid gas removal step. The solvent decomposes in corrosive products at temperatures encountered in the TEG reconcentrator. Spent TEG is typically disposed of as a chemical waste.

TEG can be reclaimed using the same CO₂ absorption technology described above for reclaiming amines. In reclaiming TEG, 400 psig steam is used. The operation uses about 650 BTU steam and 50 cu ft of CO₂ per pound of TEG. The recovered glycol is a high quality product. Total operating costs are a fraction of glycol purchase costs.

In reclaiming glycol from wellhead dehydrators, it is recommended that the glycol be removed and transported to a stationary reclaimer.

3.4.3 Saltwater-Contaminated DEA

In gas production and treating operations, saltwater co-produced with the gas may slug the treating plant inlet separators and pass through the separators. It will then contaminate the solvent used in the downstream acid gas removal operation. Chloride concentrations as high as 25,000 ppm have been reported in diethanolamine (DEA) solutions used to remove CO₂ and H₂S.

At high chloride concentrations, DEA solutions foam and cause solution losses. In addition, residual salts build up on heater tubes, causing hot spots and tube ruptures. Hot chloride-DEA solutions are also corrosive. The common solution is to remove the entire solvent inventory and replace it with new solution.

Some gas plant operators have successfully addressed this problem by removing the chlorides with a strong base anion exchange resin in its hydroxyl form. The resin takes on chloride ion and gives up hydroxyl ion.

A side-stream of the circulating DEA solution is processed downflow through a resin bed where the chloride-hydroxyl ion exchange takes place. After passing through the resin

bed, the DEA is pumped back to the main amine system. The chloride ion concentration in the treated DEA from the resin bed is checked periodically. When the chloride concentration begins to increase, the resin bed is saturated and should be regenerated.

Regeneration consists of backwashing the resin bed with water to reclassify it and then regenerating with four percent caustic solution. The bed is flushed with water to remove remaining caustic.

Theoretical chloride removal is 2.61 lbs. chloride/cu. ft. resin. For practical operation, a design factor of 0.7 is suggested. The largest operating cost item is the caustic (about 7 lbs./cu. ft. resin). Water might be a cost item; large amounts of high-purity water or condensate (2 ppm maximum hardness) are recommended. Amine solution losses amounting to 0.14 gal./cu. ft. resin can be anticipated.

Costs to install and operate any particular system are going to be highly site-specific. They will depend upon chloride concentrations, solution purchase and disposal costs, and construction.

3.4.4 Purge Streams from Sulfur Removal

A variety of processes are sometimes used to remove H_2S in small gas treating applications, typically less than 10 long ton sulfur/day. These processes may also be used in large gas plants as part of a gas treatment unit behind a sulfur recovery unit.

One process involves direct liquid phase oxidation. H_2S is absorbed into an alkaline solution that contains oxidation chemicals sodium metavanadate and the disodium salt of anthraquinone disulfonic acid (ADA). These chemicals oxidize the absorbed H_2S to elemental sulfur which is separated from the solution by froth flotation and mechanical means.

Some of the absorbed H_2S is oxidized to thiosulfate and sulfate salts. Because presence of the salts has deleterious effects on solution chemistry and corrosivity, the solution is purged when salt concentrations reach 250 gm/liter. Purging is accomplished either continuously or by dumping significant quantities of the solution inventory. A new solution must be made up to replace that which is purged. The purged solution is disposed of as a chemical waste or into a wastewater system. However, concerns about vanadium content, biological oxygen demand, and thiosulfate content are increasing disposal costs. In California, the waste is considered hazardous because of its vanadium content.

Refineries have a similar disposal problem when liquid phase oxidation is used for gas treatment. Gas treating plants that employ the process in conjunction with a sulfur recovery unit can consider the alternatives described in Section 4 as well as those presented below. The alternatives presented here are primarily applicable to small units, particularly those that do not operate in conjunction with a sulfur recovery plant.

3.4.4.1 Reclaiming/Recycling

The purged streams can be sent to a metal recovery plant. The plant receives and processes purge solution, recovers vanadium, oxidizes ADA, and converts thiosulfate to sulfate. The vanadium is sold as vanadium oxide.

The processing facilities are part of a plant designed to recover molybdenum, vanadium, aluminum, nickel, and cobalt from spent catalysts. The plant uses autoclaves, reactor tanks, thickeners, and filters for hydrometallurgical processing.

3.4.4.2 Conversion to Chelated Iron Processing

During the last ten years there have been important developments in the use of chelated iron chemistry for removing H_2S from gas streams. Some sulfur removal systems are now being converted to or replaced by a process using this type of technology. Chelated iron processes exhibit an order-of-magnitude lower production rate of by-product salts and yield a nontoxic solution that can be disposed of as a nonhazardous waste. The performance capability of chelated iron processes for removing H_2S is basically the same as that of traditional oxidation processes.

One of the chelated iron processes uses chelating agents to keep iron in solution. The H_2S is absorbed into a circulating solution where it is oxidized to elemental sulfur by the reduction of the iron. The iron is reoxidized in an air-blown oxidizer. The chemistry is similar to that of the vanadium-ADA process except that the oxidation-reduction functions provided by vanadium and ADA compounds are now provided by iron. The process has been used commercially and is considered a proven technology.

In 1987, a new chelated iron process that employs significantly higher iron concentrations came into use. The chemistry is the same except for differences in the use of chelating compounds. Because iron concentrations are so much higher, this process features markedly lower circulation rates and different gas-solution contacting equipment. The gas-solution contact device is described as a "pipeline contactor."

3.5 Miscellaneous Used Materials

A typical production operation will generate a wide variety of miscellaneous small volume wastes that need proper management to reduce cost and comply with local regulations. Examples of these wastes include empty drums, used oils, and used batteries.

3.5.1 Empty Drums

Reduction of waste drums is accomplished through changes in purchasing procedures, testing and reclassification of the residuals remaining in the drums, and on-site pH

neutralization of residuals in the drums. These procedures require coordination by those responsible for purchasing, accounting, environmental, and operating functions.

One minimization strategy is to change purchasing policies. Substitutes for hazardous chemicals that are purchased in drums are evaluated with the intent of replacing those chemicals with nonhazardous substitutes. Purchasing policies and instructions can be restated to require the use of the new nonhazardous chemicals.

Suppliers who recycle their own drums through a deposit system can be chosen over vendors who refuse to take back empty drums. In addition, purchase of materials in bulk is emphasized in lieu of drums. If bulk purchase creates a problem in outlying areas because of small usage, a central bulk storage area can be set up and an ongoing system to refill and distribute drums to the outlying areas can be implemented.

Another important part of this program can be to provide instructions for capping and segregating of drums after use. This practice has the added benefit of segregating drums that do not contain hazardous waste so they can be recycled as nonhazardous.

Another waste minimization practice entails neutralizing any acid and alkaline residues in certain drums on-site. A tank containing recyclable wash water can be used to rinse and remove both the acid and alkaline residues using a hose and catch basin that flows back into the wash water tank.

A final pH adjustment to assure compliance with water discharge requirements will be made on the wash tank. After testing verifies that there is no other hazardous material in the tank, the tank contents can be drained to the produced water system. The length of time the tank can be operated will be determined by monitoring pH and solids build-up. The rinsed drum is then recycled to a drum recycler as nonhazardous. On-site pH neutralization in fixed equipment may require a local permit.

3.5.2 Used Oils

A typical production field generates an array of intermittent waste oil streams, which can originate from such equipment as:

- Diesel driven engines
- Large equipment gear boxes
- Waste lube oils from vehicles
- Compressor lube oils

Some source reduction of these wastes has been possible through lube oil testing rather than draining of lube oils at arbitrary time intervals. Lube oil suppliers provide testing programs for field use which maximize the useful life of lube oils. Note that the regulation of used oil is in flux. Please consult federal, state, and local regulations.

Exploration and Production Waste Minimization

Case Study 3-1: Filter Press

Introduction

A West Coast production facility concerned about the cost of waste disposal evaluated several mechanical phase separation technologies. To reduce the amount of oily sludges disposed, a filter press was evaluated to segregate the oily waste into two phases, filtrate and cake. The filtrate would be further separated. Oil would be recovered from the filtrate and recycled to the crude. The water would be injected into the producing formation. The cake would eventually be disposed in an approved nonhazardous landfill.

Description of the Waste Minimization Process

Sludges from various process units and tanks were collected in a centralized tank. The oily sludge tank was kept agitated to prevent solids from settling. The sludge was pretreated with ferric chloride and lime, mixed and heated to 170 degrees F in a separate tank, and pumped to the 1500 mm press. The press was operated 24 hours a day, 350 days a year, approximately 9 cycles per day.

Effectiveness

The evaluation concluded that the filter press would reduce the volume of waste actually disposed from 44,900 barrels per year to 13,500 barrels per year or nearly 70%. Similarly, the weight of the material disposed was reduced by 62% from 9900 tons to 3700 tons per year, thereby decreasing annual disposal costs by \$564,200 per year, inclusive of trucking costs. Additionally, approximately 81% of the oil in the sludge was recovered. At \$15 per barrel, revenue from recovered oil represented an additional savings of \$108,000 per year.

Costs

The capital cost for the filter press was estimated at approximately \$3,000,000. Annual operating costs for the press were estimated at approximately \$400,000 per year, including maintenance, chemicals, labor, and power.

The reduced volume of sludge decreased disposal costs by \$564,000 per year. Oil recovered from the sludge was valued at \$108,000 per year. The net savings is \$272,000 per year. A cash flow analysis of the new system versus the old system was computed using a 12% discount rate and a 25% per year escalation in waste disposal costs. This analysis indicated that the capital cost of the new system would reach payout in 3.5 years.

4 Refining Waste Minimization Practices

This section of the Compendium contains a description of practices that can be used to minimize the generation of wastes and residuals produced by petroleum refinery operations. The waste minimization practices can be categorized as source reduction, recycling, or treatment. Some involve construction of capital equipment. Others may be implemented by changing operating or maintenance procedures.

Not all of the practices discussed in this section can be applied to all refineries. Every refinery is unique with a somewhat different process configuration and varying crude oil feedstock. As refinery configuration and crude characteristics vary, so will the applicability, effectiveness, and practicality of the waste minimization practices.

The wastes and residuals that are addressed in this section are:

- Oily sludges
- Tank bottoms
- Fluid Catalytic Cracking Unit (FCCU) decant oil sludge
- Leaded tank bottoms
- Stretford purge
- Empty drums
- Waste oils
- Solvents and chemicals
- Spent caustics
- Spent clays
- Sandblast media
- Hydrofluoric alkylation sludge
- Cooling tower blowdown
- Miscellaneous wastewater systems residuals

4.1 Oily Sludges

One of the higher-volume hazardous wastes generated by petroleum refineries is oily sludge. Oily sludges include the following:

- Slop oil emulsion solids
- Leaded tank bottoms
- API separator sludge
- Dissolved Air Flotation (DAF) float
- Heat exchanger bundle cleaning sludge

In addition to the above wastes, the category of oily sludges includes such wastes as tank bottoms and sludges which settle out in pond impoundments, drainage ditches, and sewer systems.

Oily sludges are emulsions formed because of a surface attraction among oily droplets, water droplets, and solid particles. If the solids are large and/or dense, the resultant material will settle and become a sludge. If the solids are smaller or less dense, the solid surface may result in a neutrally buoyant emulsion that will not settle.

The surface charge interactions between the solid particles and oil droplets cause the sludge to become stable and difficult to separate. Once stabilized, the sludge can be separated into its individual components by mechanically removing the solids or by neutralizing the surface charge on the solids and oil droplets.

All refinery emulsions are stabilized by solids and enhanced by surfactants that increase the attraction between oil droplets, water droplets, and solid particles.

Neutralizing the surface charge of an emulsion or sludge, using emulsion-breaking polymers alone, is almost impossible to accomplish on a continuous basis. The density and charge strength of emulsions will change almost daily, depending on the type of crude run and the quantity and type of surfactants and solids that are released into the refinery sewer system. One of the most effective ways to minimize the generation of sludges is to minimize the release of solids and surfactants into the refinery wastewater system. Other effective practices involve the use of equipment to recover oil for recycling, recycling of the entire sludge, and the following:

- Desalter Brine treating
- Filtration
- Centrifugation
- Thermal treatment
- Sludge coking

A brief discussion of each of these waste minimization practices for oily sludges follows.

4.1.1 Control of Solids into Wastewater System

Control of solids releases into the refinery wastewater sewer can be a very effective means of minimizing the generation of oily sludges. The solids content of refinery sludges varies from less than 5 percent to up to 30 percent. Using an example of a sludge that contains 10 percent solids, a reduction in one pound of solids released into the sewer system will eliminate the generation of 10 pounds of sludge. Therefore, the incentive for controlling solids releases into the wastewater system is significant. Minimization practices that can be used to reduce the quantity of solids released to refinery sewers include:

- Runoff control
- Control of exchanger bundle cleaning solids
- Control of FCCU and coker fines
- Minimization of fine solids recycling

4.1.1.1 Runoff Control

Stormwater runoff washes dust and surface solids into drainage collection basins. The runoff can come from large open areas around tank farms, fields, areas around maintenance shops and other buildings, process area equipment, and from roads that run throughout the refinery. Some newer refineries contain discrete sewer systems to handle process water separately from utility and stormwater runoff. Older refineries without segregated sewers will receive the greatest benefit from runoff control.

Runoff control practices being implemented by refiners to control solids releases include:

- Planting ground cover
- Paving/dust control
- Partial sewer segregation
- Use of a street sweeper
- Cleaning ditches

Much of the entrained solids in storm runoff results from surface dirt and dust. In most areas of the country that experience heavy intermittent rains, a considerable quantity of solids can be washed into the sewers. If ground cover is planted in areas around ditches, tank dikes, and nonprocess areas, it will act as a retainer to prevent solids from being washed into the sewers. The ground cover should be dense to provide maximum effectiveness.

Another option is to pave roads, ditches, and other areas so that the exposed soil is covered and will not add solids to the water in the sewers. To effectively reduce solids being washed into the sewer system, however, paved areas must be kept clean. Otherwise, dust and dirt that accumulate on roads during dry periods will be washed into sewers. In addition, runoff solids, particularly from a very heavy storm, will partially settle in ditches. The next storm will re-entrain some of the solids, and they will periodically settle and be re-entrained as they work their way through the refinery wastewater system. For that reason, once a road or ditch has been paved, vacuum systems or other types of street cleaners should be used periodically to keep the areas free of solids that might be washed into the sewers during a storm. Street cleaners can be operated by refinery maintenance staff, or the service can be purchased.

In some refineries, partial sewer segregation may be possible. There are typically large open areas around tank farms. Some refineries have open fields for future expansions. Runoff from these areas may eventually be routed to the process wastewater system.

Some of these areas may be isolated and routed to a stormwater impoundment where the water can be retained and tested prior to discharge in accordance with appropriate permits under the regulation on stormwater discharges.

Some refineries have several impoundments downstream of biological treatment for storage. One of these impoundments could be isolated and used to impound the stormwater. Where it would be impractical to completely retrofit a segregated stormwater system, it may be possible to isolate, into a separate system, selected streams that provide drainage for many acres. In addition, tank farms can be drained slowly after storms to prolong storage and minimize flow to the wastewater system. In some cases, separate direct discharges can be installed when water quality is good.

4.1.1.2 Control of Exchanger Bundle Cleaning Solids

Heat exchanger bundle cleaning solids constitute a RCRA-listed hazardous waste. Such solids are produced by cleaning heat exchanger bundles with high pressure water during unit maintenance, typically on a concrete pad that has been prepared for this purpose. In many refineries, the water and entrained solids are released into the refinery wastewater system. In such cases, the mixture of wastewater and heat exchange solids is not defined as a hazardous waste (see 40 CFR 261.3(a)(2)(iv)(C)).

One problem, however, is that exchanger solids may attract oil as they move through the sewer system and may also produce finer solids that are more difficult to remove. Some refiners have installed concrete overflow weirs around the surface drains on the exchanger bundle cleaning pad or have covered the drains with a screen to remove the solids from the pad. The solids must then be treated and disposed of in accordance with applicable requirements. The use of overflow weirs will probably have a minor impact on the overall quantity of sludges generated at a refinery. It may, however, reduce the generation of fine solids-stabilized emulsions that are difficult to treat.

It is best to prevent solids from forming, if possible. One widespread practice is the use of antifoulants on the heat exchanger bundles. Because antifoulants stop scale from forming, they are effective in reducing/eliminating exchanger cleaning sludge and minimizing the formation of a listed waste.

Chemical cleaning of the heat exchangers is another practice that can reduce sludge. These chemicals generate a solution allowing for the recovery of oil, thus reducing the volume of sludge. The chemicals generally can be reused.

4.1.1.3 Control of FCCU and Coke Fines

Fluid Catalytic Cracking Units (FCCUs) and delayed coking units both handle solids on a routine basis. The area around the equilibrium catalyst and the fresh catalyst hoppers in the FCCU can contain catalyst that has spilled during loading/unloading operations.

The area around the reactor and regenerator vessels can contain a significant quantity of catalyst during unit maintenance when both of these vessels are opened and cleaned for inspection and repair. Coking units can also have coke fines on the pad around the unit or in a coke storage building.

The simplest minimization practice is to instruct operations/maintenance staff to sweep catalyst and coke fines dry for recycling purposes. To make this practice effective, the refinery staff must understand its impact on waste management costs and refining economics.

An alternative method of removing catalyst and coke fines is to use a central vacuum system similar in concept to those used in homes. A building adjacent to the process unit pad would contain an explosion-proof blower and a small baghouse. Ducts would be run to dusty areas of the process unit with specified locations where sections of hose could be connected to the system to vacuum the solids. The bags would be removed periodically and sent either to recycling or to nonhazardous disposal. FCCU catalyst could be recycled to a cement manufacturer as discussed in Section 4.9.2. The coke could be recycled for fuel use.

As a result of weathering and wind, coke piles, conveyors, and transport of coke can also be a source of coke fines. Dust control chemicals applied to the coke will often reduce dust and migration of coke fines.

4.1.1.4 Minimizing of Fine Solids Recycling

As previously discussed, solids attract oil and water which results in the creation of an emulsion or a sludge. In addition to minimizing the release of solids into the wastewater system, solids should also be purged from the system.

Refineries typically have a solids recycling system that cannot be totally bypassed (see Figure 4.1-1). Solids enter the refinery with the crude charge as part of the bottom sediment and water (BS&W). The electrostatic desalter located on the crude unit should remove most of the solids, salts and water present in the crude oil.

Minimizing the introduction or recycling of solids or fine solids into the slop oil recycled to the crude unit of Figure 4.1-1 will assist the reduction of these sludges. The solids will attract more oil and produce additional emulsions and sludges. The following waste minimization practices can help reduce solid levels:

- Reduction in the quantity of crude tank bottoms sent to the desalter.
- The use of a low shear mixing device to mix desalter wash water and crude.

- Avoiding turbulence in desalter vessels by using lower pressure water.
- Breaking the fine solids recycle loop between the wastewater and slop oil treating systems.
- Treating DAF float separately, rather than sending it to the slop oil system.

Treating desalter brine at the crude unit before its release into the wastewater system is another alternative for removing sludge (see Section 4.1.3).

Some of these practices can be particularly beneficial with certain crude oils. Crudes produced in the San Joaquin Valley of California tend to have a high concentration of surface-active organics, such as naphthenic and cresylic acids. When turbulently mixed with fine solids, these organics will produce emulsions.

Solids can settle out in crude storage tanks. If solids in crude storage are allowed to settle in the crude tanks, they do not add to solids loading in the desalter. Settling in the crude tanks also prevents these solids from eventually becoming listed as either API separator or slop oil emulsion solids. Infrequently, these tanks must be removed from service and cleaned. Crude tanks can be cleaned using heat and chemical treatments such that the oil in the solids can be recovered and run as slop, the water can be drawn off to the waste plant, and residual solids can be removed and disposed of in accordance with applicable requirements. (See also 4.2 on tank bottoms.)

An alternative that can increase the time between tank cleanings is to use static or variable angle tank mixers to homogenize the crude fed to the desalter.

High-shear mix valves used in many crude units to mix wash water and crude oil will create an additional emulsion. Low-shear, in-line static mixers or other low energy mixing devices will aid in the reduction of emulsion generation.

Solids that have settled in the desalter vessel must be moved to a boot where they are typically transferred to the wastewater sewer. Some desalters, however, contain high-pressure water jets that move the solids. Depending on the water spray angle and velocity, the spray can pick up solids from the desalter bottom and move them upward toward the oil/water interface. This process adds mixing to a vessel that should be kept quiescent, and it may create additional emulsions. Consideration should be given to replacing water jet sprays with mud rakes that move the solids without adding turbulence to the vessel.

Figure 4.1-2 shows a scheme for integrating sludge-treating equipment into refinery wastewater and slop oil systems to purge fine solids thereby reducing active solid sites

that can form an emulsion. In this example, the sludge-treating unit receives all of the solids-containing slop oil streams prior to slop oil treatment. A plate and frame filter press of the type described in Section 4.1.4 is particularly effective for this application. With the solids removed, the oil and water will separate. The solids that would normally be recycled are purged from the system with the filter cake. Significant savings can result from the elimination of slop oil-treating chemicals.

4.1.2 Control of Surfactants in Wastewater System

The uncontrolled or unnecessary addition of surfactants to the refinery sewer system will tend to increase the generation of emulsions and sludges. Surfactants cannot be eliminated from the system, but they can be effectively managed.

Surfactants such as naphthenic and cresylic acids occur naturally in crude oil. Surfactants present in desalter wash water will be released into the wastewater system at that point. Another source of surfactants is spent phenolic caustic produced by treating gasoline. Other surfactants that can be present in wastewater systems include detergents used to wash unit pads; equipment; and vehicles and organic polymers used to break emulsions or otherwise aid in oil/water separation.

One mechanism is to avoid the introduction of surfactants into an oily wastewater stream immediately upstream of a high-speed centrifugal pump. The shear in the pump will promote mixing of the solids and oil with the surfactant which will facilitate the formation of emulsions and sludges.

The effective minimization of surfactant releases into a refinery wastewater system will require a well planned and well communicated training program for operations and maintenance personnel.

Potential surfactant sources addressed in this compendium include:

- Unit pad detergent washing.
- Use of surfactants in wastewater system.
- Spent caustic produced by treating naphthas with an end point of over 400 degrees F.
- Vehicle cleaning.
- Miscellaneous soaps and cleaners used in lab and maintenance shop.

Detergents are sometimes used to clean oil stains and dirt from process unit concrete pads. Dirt should be swept up dry and removed. Detergents are usually necessary to maintain a safe working environment. However, their use in each plant should be reviewed carefully, and operators should be instructed to minimize the quantities used. Often, high-pressure water with steam can achieve satisfactory cleaning results without detergents.

Organic polymers are used in the wastewater system to aid in separating oil, water, and solids and to break emulsions. Polymers can be used in the following locations:

- Desalter feed to aid in oil/water separation.
- Dirty desalter wash water to separate some oil from the water prior to release in the wastewater system.
- API separator feed and/or air flotation unit feed to assist in oil/water separation.
- The slop oil treating unit to assist in breaking the emulsion and enhancing oil/water separation.

Although polymers are required to achieve optimum separation of oil/water/solids mixtures, the use of any one polymer must be carefully monitored to avoid counteracting the effectiveness of other polymers employed elsewhere in the wastewater system. Process engineers should attempt to minimize polymer usage because negative effects more commonly result from overuse of polymers than from under use.

Chemical vendors should justify every polymer used, and the responsible engineer should know the type, function, and recommended dosage of all polymers. Operators should also be trained to minimize polymer usage.

Another source of surfactants in a refinery wastewater system is spent phenolic caustics produced by treating gasolines with an end point of over 400 degrees F. Above this temperature, the concentration of acid oils such as phenolics, cresylics, and naphthenics increases significantly. These surface-active materials will function much like detergents to stabilize emulsions.

Spent phenolic caustic can be sold to a recycling organization that will recover the acid oils or the acid oils can be recovered at the refinery (see also Section 4.8).

Detergents are also used to clean tank trucks at the product loading rack and to wash company vehicles. In some refineries, it may be possible to route the wash water from the truck rack to a point downstream of the air flotation unit. In cases where the locations

of these two operations are too far apart, the personnel responsible for washing trucks should be trained to minimize detergent usage.

4.1.3 Desalter Brine Treating

In some refineries, the desalter can add a significant quantity of oil and solids to the process wastewater system. Desalters in refineries with crude charge rates that have increased significantly over the years may tend to accumulate more oil in their wash water if the desalter vessel is undersized for current crude charge rates.

Solids content of desalter wash water is a function of feedstock, refinery configuration, and desalter operating mode. Even though a refinery continuously uses mixers to suspend settled material from the crude charge tanks and feeds the suspended solids to the desalter, there may be brief periods when the solids load from the desalter to the sewer is very high owing to the intermittent operation of the desalter's solids purge system.

Desalter brine produced at most refineries will not benefit from pretreatment; however, certain refineries that process heavy crudes with a specific gravity that approaches water, crudes with a high concentration of natural surfactants, and crudes with a high solids content, may benefit from desalter brine treatment.

Pretreatment of desalter brine prior to release to the process wastewater sewer may be undertaken to:

- Reduce solids load into the process wastewater sewer.
- Destabilize and separate the oil/water/solids emulsion present in desalter brine before it contributes to formation of additional emulsified material in the sewer.
- Reduce oil load to the wastewater sewer.
- Reduce the concentration of certain soluble organic constituents present in crude oil that may present treatment or discharge problems if not treated at the source.

Figure 4.1-3 shows a process flow sketch for a desalter brine treating unit. This system would treat a highly emulsified brine from processing a very heavy crude. All of the chemicals shown would not always be required.

The brine is first mixed with a naphtha to reduce the relative density of the oil so that it will separate faster. This treatment is useful for crudes with an API gravity close to that of water. If there is an emulsion in the brine, organic polymers can be used to aid in

breaking the emulsion; however, the performance of such polymers may vary considerably as crude characteristics change (See Section 4.1.2).

If considerable emulsified material is present in the brine and polymers are found to be ineffective, then the surface charge on the solids can be neutralized by adding acid to reduce the pH to around 2.0. The reduced pH, along with the addition of naphtha, should allow a relatively good separation of the oil, water, and solid phases.

The chemical additives are mixed with the brine prior to its being sent to a separator vessel. Figure 4.1-3 shows a separate mixer vessel with slowly moving paddles, but an in-line static mixer can also be used. The mixing device must provide the desired contact with minimal shear to be effective.

The separator vessel can be a simple one, sized to provide the residence time needed for phase separation. A corrugated plate separator can be installed in the vessel to increase greatly the effective residence time. Two refineries have used a separator vessel that contains electrical equipment similar to the electrostatic desalter. The electrostatic field maintains a sharp oil/water interface and assists in the phase separation process.

In some cases, solids can be withdrawn with the water from the bottom of the vessel.

4.1.4 Filtration

Filtration is a mechanical separation technique that is very effective for reducing waste volume and for recycling oil. Filtration is attractive for listed wastes because it is convenient to implement, it reduces waste volumes, and it can be permitted readily in most areas. Belt filter presses, recessed chamber pressure filters, and rotary vacuum filters are described in detail below.

4.1.4.1 Belt Filter Press

A belt filter operation consists of a belt filter press, upstream facilities to handle and condition oily waste, and downstream facilities to separate oil and water and take away the filter cake. Figure 4.1-4 is a block flow diagram for a belt filter installation.

A high molecular weight polymer (polyelectrolyte) is normally added to the sludge prior to filtration in a belt filter in order to neutralize the electrochemical forces that bind the emulsion, promote the release of oil and water, and coagulate the solids.

Initially, the raw feed is mixed with a polymer to cause flocculation of solids and enhance separation of the liquid phase. The preconditioned feed is then distributed to a porous, woven belt where the gravity phase of liquid/solids separation occurs. Free liquid flows through the porous belt by gravity into filtrate collections pans. Up to 40 percent of the

liquid phase of the feed can be removed in the "gravity zone." The porous belt with the gravity-separated solids on it is then enveloped by another belt as it leaves the gravity zone and enters the low-pressure or "wedge zone", where further phase separation is achieved using mechanical pressure. In the third zone, the belts pass through a series of large rollers that squeeze the belts together, forcing additional liquid through the porous belt into filtrate collection pans. Manufacturers report that pressures can reach 14.2 pounds per square inch or more in the high-pressure zone as the belts travel through a series of rollers. The final liquids separation occurs owing to high pressure and shear forces between the two belts as they travel over the rollers. Pressures in the second and third zones are generally adjustable. The deliquified sludge cake is scraped off the belt into a container for disposal. A high-pressure water wash is usually applied to the belt at this point to clean it and to unplug clogged belt pores.

Behavior of the sludge in the free-draining section is strongly dependent on the composition of the feed. Sludges with low solids content and low-viscosity oil tend to be very fluid. Such sludges may require some means of separating liquids ahead of the filter. For example, the sludge may be held in a tank for a specified period to break up some of the emulsion and to drain off some of the separated oil and water. Heat is usually applied to speed up the process. Removal of oil and water in a pretreater will keep the size of the filter to a minimum.

Belt filters produce a filtrate that can be separated into oil and water phases. The oil is recycled to the refinery, and the water is drained to the wastewater treatment unit.

The cake from a belt filter is typically 25 to 40 percent solids. Depending upon the solids content of the oily waste, the operation can produce substantial volume reduction. With typical refinery oily sludges, the oil content of belt filter cake is usually 10 to 25 percent.

The cost for a belt filter installation can fluctuate widely, depending upon the owner's approach to system design and utilization. Net operating costs are almost always a net revenue (or savings) when the value of recovered oil is credited. Chemical, utilities, labor, and maintenance costs are highly dependent on size and use. Actual return on capital investment is dependent on the size and configuration of the filter press and the level of utilization.

4.1.4.2 Recessed Chamber Pressure Filter (Plate Filter)

A recessed chamber pressure filter uses hydraulic pressure and a separation medium to separate liquids and solids. Figure 4.1-5 is a block flow diagram for a sludge-treating installation based on the use of a filter.

A recessed chamber pressure filter, also called a plate filter or plate and frame, is made up of a number of parallel filter plates. Figure 4.1-6 is a cross-sectional representation of a plate filter. The plates are stacked next to one another in series arrangement and

held tightly together by a hydraulic piston. They are fabricated to provide a series of chambers in which solids may collect. Each plate is covered with a filter medium, (e.g., cloth).

Sludge is delivered to the chambers by means of a positive displacement pump. Liquids pass through the filter medium and are collected for later treatment while solids are collected inside the plate chambers. It is normal practice to treat the sludge with conditioning chemicals before it is fed to the filter.

The filter medium is precoated with material such as diatomaceous earth at the beginning of each cycle. Precoating alleviates blinding of the medium by fine solids during operation and also promotes release of the collected solids from the press at the end of the cycle.

To filter oily sludge effectively, the sludge must be preconditioned by heating and adding chemicals in order to destabilize emulsions and increase filtration rate. In filtering oily sludges, ferric chloride and hydrated lime are typically used as conditioning chemicals. Amounts added are dependent upon the amount of solids present in the sludge. Normal practice is to add predetermined amounts of ferric chloride and lime for every pound of solids contained in the sludge.

Pressure filtration can be highly effective. A well-run operation can produce a cake having 50-60 percent solids and less than 10 percent oil.

The cost for a pressure filter installation can fluctuate widely, depending upon the owner's approach to system use. Some operators may choose to operate this type of equipment 1 shift/day, 5 days/week, while others may elect to operate continuously. Net operating costs are almost always a net revenue (or savings) when the value of recovered oil is credited. Actual return on capital investment is dependent on the size and configuration of the filter press and the level of utilization.

4.1.4.3 Rotary Vacuum Filter

A vacuum filter is a cylinder with two closed ends. The surface of the cylinder is covered with a filter cloth and partly submerged in a tank containing the slurry to be filtered. In operation, the cylinder is rotated slowly on its axis while a vacuum is applied to its inside. Filtrate is pulled through the filter cloth while the solids contained in the sludge are deposited on the surface of the cylinder. Deposited solids are scraped off with a scraper and removed for disposal as the drum rotates. Filtrate is collected and delivered to a treatment module via a pump. See Figure 4.1-7 for a block flow diagram.

A vacuum filter is operated in a semi-continuous manner. A thick layer of diatomaceous earth or some other filter aid is deposited on the surface of the filter drum at the beginning of a filter cycle. During operation, the scraper removes a very thin layer of

precoat with the filtered solids for every drum revolution. Filtration is stopped when a predetermined thickness of precoat has been removed, and a new precoat layer is redeposited on the drum.

A precoat system consists of a storage facility for dry precoat material, a tank for preparing a water slurry of the material, a feeder for feeding the dry precoat to the slurry tank, and a pump for transferring the slurry to the filter. A precoat recycle pump sends the filtrate water back to the slurry tank during precoating. The cost of the precoat module is determined by the size of the filter.

A vacuum filter installation requires upstream and downstream facilities much like those for pressure type filters. In terms of performance, a vacuum filter is more like a belt filter than a pressure filter. Solids content of the cake will be about 30 percent. Oil recovery in the filtrate is less, because the diatomaceous earth precoat tends to absorb it.

Cost for a vacuum filter installation will fluctuate widely, depending upon the owner's approach to system utilization.

4.1.5 Centrifugation

Centrifugation, like filtration, is a mechanical treatment technology used to recover oil and reduce waste volume. Centrifugation is typically an alternative to filtration, and a decision on which to employ is based on application-specific criteria regarding cost, performance, and operating characteristics.

In centrifugation, the rapid spinning of a cylindrical container, forces the denser materials toward the outer wall of the cylinder where they can be removed. The force applied is generally several thousand times the force of gravity. Centrifuges used in the petroleum industry are scroll and disc type machines, both of which run continuously.

4.1.5.1 Scroll Centrifuges

Horizontal and vertical scroll centrifuges are commonly used centrifuge systems. A horizontal scroll centrifuge is shown in Figure 4.1-8. The feed is introduced into the center of the bowl, where the centrifugal force causes the material to separate into light and heavy components. The heavier materials, solids, are forced to the outside of the bowl, where a helical scroll conveyor moves them down the bowl toward one end and out the discharge. The liquid travels in the opposite direction in the bowl, flows over a weir, and is then withdrawn from the centrifuge. The operation of a vertical machine is similar except it is suspended vertically from one end instead of mounted horizontally.

Horizontal scroll centrifuges are capable of separating sludge into a solid and either one or two liquid streams. A machine producing only one liquid phase is referred to as a two-phase machine. The combined oil/water stream could be separated in an existing

slop oil treating tank or in a new tank built as part of the treatment system. The three-phase scroll machine produces separate oil and water phases. Oil can travel to the slop oil system, or possibly even to crude charge, and water can go to the refinery oily waste sewer system.

Vertical scroll machines operate much like horizontal units. Solids move to the outside of the bowl and out the bottom, and liquid goes to the top. Vertical scroll centrifuges produce only one liquid stream; therefore, a downstream oil water separation tank is required. Vertical centrifuges cost 35 to 50 percent more to manufacture than horizontal machines of the same capacity owing to the mechanism required to suspend the bowl in a true vertical position. Vertical machines are generally only used for temperatures above 200 degrees F, at high pressures, or where space is a consideration.

Centrifugal force developed by various manufacturers' machines is usually measured relative to the force of gravity. In general, horizontal and vertical two-phase scroll centrifuges will produce a force about 3,000 times the force of gravity. A horizontal three-phase scroll machine will produce a force about 2,400 times that force of gravity. According to manufacturers, horizontal two-phase scroll units should produce a dryer solid than the three-phase units owing to their higher force.

4.1.5.2 Disc Centrifuge

Figure 4.1-9 shows the operation of a disc centrifuge. Machine designs allow the feed to be introduced either into the top or the bottom. The feed liquid is led outward and up through a hole in each disc, and the three components of the feed are separated by the high centrifugal force developed by the rotation of the bowl. Disc centrifuges can produce a force up to 7,000 to 9,000 times that of gravity.

Narrow spacing between the discs provides a shortened path for conducting light-phase liquid to the center of the bowl and out through the discharge port. Solid particles and heavy liquid are sent to the outside of the bowl. A small part of the heavy-phase liquid is used to flush the solids through the nozzles, while the remainder is conducted upward and discharged through a port at the top of the bowl. Disc centrifuges fit best as the second stage in multiple-stage centrifuge systems. A first-stage scroll centrifuge is used to remove the majority of the solids, particularly the larger ones. A higher-speed disc centrifuge is used to increase the capture of fine solids and to help achieve a good phase separation of water and oil. In this configuration, the solid slurry that is produced out the side of the disc centrifuge can be returned to the scroll machine, possibly after solids flocculation.

4.1.5.3 System Design

Although single scroll-type centrifuges can be used to treat sludges, in some circumstances this centrifuge may not produce a refineable oil, a relatively clean water,

and a solid that does not contain free liquids at the same time. Fine solids not recovered with the cake tend to form an emulsion in either the oil or water phase. A single centrifuge would be effective if the objective is to remove liquids so that the resultant oily solids could be fed to a coker, treated, or incinerated.

Effective chemical treatment of the feed is more important with centrifuges than with filtration systems, where solid particles are removed from the sludge because of their size. In a centrifuge, the density difference between the liquid and solid phases separates the sludge. If a solid particle denser than water is coated by an oil droplet less dense than water, the oil-coated particle may be neutrally buoyant and not separate effectively in the centrifuge. Successful centrifuge operations use de-emulsifiers in an attempt to water-wet the surface of the solids.

Fine solids can be particularly troublesome because they do not have sufficient mass to separate in the centrifuge without significantly decreasing the throughput of the machine. For smaller particles, a longer residence time is required, and the potential of the machine to achieve the desired performance is lower.

Capital costs of centrifuge systems can be less than those of pressure filter installations but greater than those of belt or vacuum filter installations. Operating costs almost always turn out to be a positive cash flow (i.e., savings) if recovered oil can be credited.

4.1.6 Thermal Treatment

Thermal treatment is used to achieve maximum volume and toxicity reduction short of incineration. In some applications, thermal treatment methods can meet BDAT treatment standards. At the same time it maximizes oil recovery.

Figure 4.1-10 shows a block flow diagram for a thermal sludge treatment installation. Typically, oily sludges are processed ahead of thermal treatment for bulk removal of liquids.

A thermal processor vaporizes the volatile components in the feed, leaving behind a dry, solid residue. The feed is heated to approximately 350 to 500 degrees F to vaporize the water and volatile organic compounds that can be stripped at this temperature.

The feed system to the thermal processor consists of conveyors, a feed hopper, and a rotary valve to introduce the cake into the processor.

A screw conveyor-type thermal processor is illustrated in Figure 4.1-10; it is an essentially closed system equipped with a rotating screw or paddle device inside to move the material being processed along the length of the unit. Hot oil is circulated through passages inside the screw and walls of the unit to supply the heat needed. The procedure for sizing a thermal processor is similar to that used for sizing a heat

exchanger. The hot oil that supplies the heat is heated in turn with a fired, hot oil or electric heater.

Solids leaving the thermal processor are hot and can be dusty. Solids handling facilities use a conveyor to transport the material and can be equipped with a water spray to cool the hot solid and control dust.

Figure 4.1-10 shows just one of the thermal treatment processes available. Alternative methods, such as spray drying, can also be useful in certain situations.

4.1.7 Sludge Coking

Many oily sludges generated within a refinery can be recycled to a delayed coking unit. Sludges amenable to this process include DAF float, API separator sludge, slop oil emulsion solids, and heat exchanger solids. Sludge coking permits recovery of hydrocarbons present in the sludge for recycling within the refinery, while the remaining solid material becomes part of the coke product. Delayed coker sludge technology is in commercial use at many refineries that process a variety of sludges.

Key parameters to evaluate when considering delayed coker sludge recycle technology are coke quality specifications and the quantities of sludge to be handled, relative to coke production. These parameters may limit the quantity of sludge that can be recycled.

At least three delayed coker recycle technologies are available. One process is designed to inject sludge as a quench medium directly to the coke drums during the coker quench cycle. The second process mixes the sludge with gas oil and injects the mixture into the coke drum feed line. The third process is designed to inject sludge into the blowdown contactor usually associated with delayed coking units.

4.1.7.1 Quench Water Injection

Coke quenching was developed during the early 1970's as a treatment for refinery sludges such as API separator sludge, tank bottoms, DAF float, and wastewater treatment biological solids.

Sludges are mixed with quench water at the beginning of the coker water quench cycle. (Quench water is added to a coke drum to cool the drum before cutting and removing the coke.) A large fraction of the added sludge is water and volatile organics. Water and hydrocarbons present are flashed off in large part during the early portion of the quenching cycle and recovered in the blowdown system. Solids and organics that do not vaporize are dispersed through the coke voids and become part of the petroleum coke. The quantity of sludge recycled is controlled to prevent sludge carryover and to maintain acceptable coke specifications.