## API PUBL\*302 91 WASTE MINIMIZATION IN THE PETROLEUM INDUSTRY

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## SOURCE REDUCTION

RECYCLE TREATMENT

DISPOSAL

## A COMPENDIUM OF PRACTICES

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# Waste Minimization in the Petroleum Industry a Compendium of Practices

Health and Environmental Affairs PUBLICATION NUMBER 3020

**NOVEMBER 1991** 

American Petroleum Institute



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#### 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.

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## 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.

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## 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

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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 subsections<sup>1</sup> 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.)

<sup>&</sup>lt;sup>1</sup> 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 The hierarchy consists of a series of generation and management problems. 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 hierarchial 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.

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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

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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 longstanding 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.

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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 hay
- 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  $CO_2$  absorption reclaimer may be able to effectively reclaim high molecular weight amines such as DEA, MDEA, and diisopropylomine (DIPA). Hot  $CO_2$  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  $CO_2$  is preheated by overhead heat exchange. In the kettle,  $CO_2$  absorbs solvent from the liquid surface. Solids in the amine solution are left to accumulate in the kettle. Saturated  $CO_2$  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  $CO_2$  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  $CO_2$  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  $CO_2$  and  $H_2S$ .

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

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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 odium 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

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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.

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## 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.

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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

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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 API PUBL\*302 91 🛲 0732290 0529031 159 📟

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.

A process flow diagram for quench water injection is presented in Figure 4.1-11. As of this writing, approximately 12 process units are currently installed and operational in the United States. Sludge loading rates are dependent on coke production and cooling cycle temperatures.

## 4.1.7.2 Coking Cycle Injection

Sludge conversion to the coking cycle, or flexicoker, incorporates the injection of oily refinery sludges mixed with gas oil into a delayed coker. Oily sludge is collected in a storage bin, pumped at a controlled rate to a slurry mix drum, and blended with gas oil using a mixer. The mixture is injected directly into the coke drum feed line along with the normal feed. The advantage of this processing scheme is that all components of the sludge are subject to the full coking process. The light hydrocarbons and water are flashed overhead and returned to the fractionator. Heavier hydrocarbon constituents are volatilized (some break down to shorter chain molecules which then volatilize) during the coking process. The remaining solids become part of the coke. Figure 4.1-12, shows a process flow diagram for coking cycle injection.

### 4.1.7.3 Blowdown Injection

Figure 4.1-13 illustrates the process of injecting sludges into the blowdown contactor used to separate quenching products. Sludge is first collected in a tank and then pumped to one of two possible contactor entry points. The contactor depicted has been modified by the addition of three new disk-and-donut trays. The preferred sludge injection point is below the top two new trays. A second option is to add the sludge to the coke drum vapor line immediately before it enters the contactor downstream of the desuperheater.

Once introduced to the contactor, the sludge components separate. The associated water is condensed and discharged to the sour water system. The solids and oil exit the bottom of the contactor and are routed to the delayed coker unit fractionator section where hydrocarbon fractions are recovered. Remaining sludge solids enter the coke drums and become part of the coke product.

# 4.2 Tank Bottoms

In any attempt to minimize waste in refinery operations, attention should be given to minimizing tank bottoms. Tank bottoms, which are the solid or semi-solid materials or sediment that accumulate in the bottom of storage tanks, can constitute a large percentage of waste in a refinery and often present difficulties for disposal.

Tank bottoms are composed of a combination of various constituents including solids or sand (brought in with crude oil), produced water, rust or scale (from the tank or transfer lines), and heavy hydrocarbons that sink. The rate of buildup of these materials is very slow because their concentration in the stored material is very low. Generally, several

years pass before sufficient amounts build up to a point where the tank is taken out of service to remove the bottom sediment. Tank bottoms are also removed as a standard procedure in preparation for maintenance or repairs that require welding.

The makeup of tank bottoms varies widely according to local conditions and the various hydrocarbons being stored. Tank bottoms can contain:

- Oil 40 to 90%
- Water 10 to 40%
- Solids 2 to 50%

The volume of tank bottoms varies according to tank service, years on-line, and age of tank.

Minimizing the quantity of tank bottoms during the cleaning procedure is key to reducing the amount of tank bottom waste generated. Most important, as much free oil and water as possible, even that portion below the pump suction line, should be removed before the tank is taken out of service.

Once the tank is taken out of service, it is often very cost-effective to separate the remaining oil and water phases of the tank bottom as these phases can still comprise a large percentage of tank bottoms. Some refineries operate filters or centrifuges on a routine basis to treat tank bottoms to minimize waste disposal and to recover oil. Separated oil is recycled back to the refining process, and the water phase is released to the plant sewer for subsequent treatment as wastewater. The remaining solids are managed in acceptable facilities. The centrifuge/filtration systems can be permanently installed or transportable systems can be supplied by service contractors. (See also sections 4.1.4 and 4.1.5.)

Cleaning out heavy oil and crude tanks can be especially difficult. Some tank cleaning service companies are marketing new techniques for removal of muck from tank bottoms. In some situations, it may be possible to reclaim up to 95 percent of the oil from a tank bottom and reduce up to 95 percent of the waste.

An alternative method for minimizing the amount of crude oil tank bottoms involves the use of mixers to keep the sludges continuously in suspension so that they travel with the crude oil to the refining process. Some refiners routinely use emulsifying chemicals in the crude to keep water and solids in suspension and later use de-emulsifiers in the desalters at the crude units. As discussed in 4.1.1.4, however, it may, in many cases be better to allow the solids to settle in the crude tank than have to address them in the desalter.

If mixers are to be used, various types can be placed in crude tanks. In some installations, three or four manually adjustable mixers are spaced equally around the tank

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wall. The direction of flow for these mixers is changed manually every few weeks based on experience. In another common configuration, a sweeping mixer automatically oscillates to produce a sweeping motion over the floor of the tank, so that the heavy oil and particles remain suspended in the crude.

# 4.3 Fluid Catalytic Cracking Unit (FCCU) Decant Oil Sludge

Heavy cycle gas oil from the bottom of the FCC Main Fractionator Column typically contains catalyst fines in a concentration ranging from 0.2 to 0.4 weight percent. The presence of the fines inhibits the recycling of this heavy slurry oil.

Slurry oil that is to be used as fuel or carbon black feedstock is usually sent to a tank for storage to settle solids. However, fine particles tend to remain in suspension. In addition, the tanks must be opened periodically and the catalyst sludge removed and managed as a waste.

Figure 4.3-1 shows a modular system employing 12-inch diameter carbon steel cylinders for minimizing the solids in decant oil. Each module is equipped with a 4-inch diameter tubular electrode surrounded by glass beads. As solids-laden oil passes into the separator module, the catalyst particles become polarized in the high-voltage electric field and are captured on beads. Catalyst is automatically removed by backflushing with an upward flow of oil which is returned to the FCCU for reuse.

The beads are the key to the separator's performance. The spherical beads capture particulate matter at the multitude of contact points within the separator and permit easy release of the catalyst particles during backflush. The proper type and size of beads are selected to create the high-energy field required to remove fine catalyst particles.

Solids removal operating from FCCU decanted oil has been reported at 94 percent. Removal of solids from slurry oil has been 99 percent. One refinery reports the elimination of the need for disposal of 100 tons per year of tank bottoms from the decant oil tank.

Another way to reduce catalyst in the decant oil is to install high efficiency cyclones in the reactor. This can shift the catalyst fines losses from out of the reactor to out of the regenerator where the fines can be collected in the electrostatic precipitator. On the order of two pounds of tank bottoms is avoided for every pound of catalyst exiting the regenerator instead of the reactor.

In addition, filter systems, centrifugation, and chemical treatment systems are all available for removing cat fines for ultimate recycling.

# 4.4 Purge Stream from Tail Gas Treating

A process for the removal of sulfur compounds from gas streams is used extensively in U.S. refineries to clean the tail gas emissions previously exhausted by sulfur recovery plants.

The tail-gas stream is contacted with the solution in an absorber and the hydrogen sulfide reacts to produce elemental sulfur and a reduced vanadium salt. The sulfur is separated from the solution by flotation.

Several side reactions take place which produce sodium thiosulfate and sodium sulfate. Control of these concentrations has traditionally been accomplished by purging a continuous solution stream or by changing out the entire solution inventory when the salt levels get too high. In many cases, the purge must be managed as a chemical waste at a substantial cost. Three waste minimization alternatives to reduce the waste solution include conversion to methyl diothanolamine (MDEA) designs, and use of a vanadium recovery system.

## 4.4.1 MDEA Conversion

There are a variety of MDEA processes, but they typically consist of two steps. In the first step of the process, essentially all sulfur compounds in the tail gas  $(SO_2, S_x, COS, CS_2)$  are converted to  $H_2S$ . The tail gas is heated to reaction temperature by mixing with the hot combustion products of fuel gas and air. This combustion is carried out with a deficiency of air to provide sufficient  $H_2$  and CO to convert all of the sulfur and sulfur compounds to  $H_2S$ .

The heated gas mixture is then passed through a catalyst bed where all sulfur compounds are converted to  $H_2S$  by hydrogenation and hydrolysis. The hydrogenated gas stream is cooled in a steam generator and then by direct contact with a buffer solution before entering the  $H_2S$  removal portion of the process.

The second step is the removal of  $H_2S$  from the hydrogenated tail gas. One of several processes used to remove  $H_2S$  involves absorption in a solution of MDEA or one of the recently developed highly selective amine-type solvents. The cooled, treated tail gas enters the solution contactor where  $H_2S$  is absorbed from the gas. Solution entering the top of the contactor absorbs essentially all of the  $H_2S$  and a small portion of the CO<sub>2</sub>. Any entrained amine is removed from the tail gas in a knockout drum.

Rich solution is routed to an associated regeneration system where  $H_2S$  and  $CO_2$  are stripped away. This enriched  $H_2S$  stream is then recycled to the sulfur recovery plant. Lean solution is pumped back to the solution contactor to complete the cycle. The tail gas leaving the absorber need not be incinerated to meet required  $H_2S$  and total sulfur specifications.

The pressure drop for the treated gas is 2 to 3 psi; all pressures are near atmospheric. Operating temperature is 550 to 750 degrees F for the hydrogenation hydrolysis reactor. Equipment is essentially all carbon steel. The clean tail gas contains fewer than 10 ppm  $H_2S$  when the newer solvents are employed.

The costs associated with converting to MDEA technology for sulfur removal are highly site-specific and depend upon how much of the existing equipment might be used.

## 4.4.2 ADA and Vanadium Recovery Process

A patented process has been developed to purge thiosulfate while recovering anthraquinine disulfuric acid (ADA) and vanadium to recycle them back to the tail gas system. Figure 4.4-1 illustrates this recovery process, which consists of the unit operations of filtration, charcoal adsorption, and ion exchange operating on a semicontinuous cycle. The filtration section provides a stream that contains no sulfur particles that would interfere with performance of the activated charcoal or the ion exchange resin. Porous tube filters provide essentially 100 percent removal of sulfur particles down to around 0.5 microns. If a high sulfur concentration is present in the purge solution, an additional filter may be required upstream of the porous tube filters.

After sulfur removal, charcoal adsorption removes ADA from the purge stream while ion exchange resin removes vanadium. The purge is then discharged to the sewer. Additional treatment could be provided, if necessary, to oxidize thiosulfate prior to discharge. During the loading step, chemicals are removed from the purge onto the recovery beds. After the charcoal and ion exchange beds are fully loaded, they are simultaneously regenerated.

Regeneration is accomplished using a four percent caustic solution to remove vanadium from the ion exchange resin. The effluent from the resin bed is then heated and used to strip the ADA from the charcoal. The caustic stream, containing the ADA and vanadium, is returned to the balance tank. A system flush follows to lower the pH in the resin bed and to cool the charcoal. The recovery beds are then ready to be loaded again.

This process will recover 95 percent of the ADA and between 80 to 85 percent of the vanadium. Vanadium recovery is sensitive to the thiosulfate concentration of the purge.

The system unit uses modest amounts of electricity, instrument air, cooling water, and chemicals. The steam requirement is about 1.2 lbs./gal. of feed. Condensate is 2.2 gal./gal. of feed. Caustic (25 percent strength) for regeneration amounts to 0.1 gal./gal. of feed.

# 4.5 Empty Drums

Empty drums that previously contained petroleum products, chemicals, or waste become a waste handling problem and must be either recycled or crushed and transported to disposal.

Reduction of waste drums can be 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 a significant team effort by the purchasing, accounting, environmental, and operating departments within the refinery.

Nonhazardous substitutes for hazardous chemicals purchased in drums should be evaluated, and purchasing policies and instructions should be restated to require the use of the new nonhazardous chemicals.

Purchases should be made from suppliers who recycle their own drums through a deposit system rather than from vendors who do not take back empty drums. Furthermore, purchase of materials in bulk should be required in lieu of purchasing material in drums. If purchase in bulk creates a problem in outlying areas because of low usage, a central bulk storage area can be set up and a system to refill and distribute drums continually to the outlying areas can be implemented. Some vendors are phasing out the sale of chemicals in drums. Chemicals not sold in bulk are sold in reusable, returnable containers.

Another important part of this program is to provide instructions for capping of drums after use so that workers do not inadvertently use them for disposal of unknown materials. This policy has the added benefit of segregating drums that do not contain hazardous waste so they can be recycled as nonhazardous.

Another minimization practice is to neutralize 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 residues and alkaline residues using a hose and catch basin that flows back into the washwater tank.

# 4.6 Slop Oils

A typical refinery generates a broad array of intermittent slop oil streams originating from either operations or maintenance activities. Slop oils represent a large volume of recyclable materials in refineries and taking advantage of this can significantly decrease waste generated in many refineries.

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Examples of operational waste oils include:

- Off-spec products
- Off-spec intermediate streams
- Oil/water separator skimmings
- Oil in ballast water
- Startup or shutdown streams
- Laboratory samples
- Product sample tops

Examples of maintenance slop oils are:

- Drains from refining vessels prior to maintenance
- Used lube oils from vehicles and equipment
- Hydraulic fluids from heavy equipment
- Compressor lube oils

These wastes represent a negative impact on operating earnings of a refinery and are being minimized because of economic pressure to reduce operating costs. Source reduction of some of these wastes is possible through training and educational programs. Slop oil streams of significant volume are frequently pumped directly to a slop oil tank where they are treated and ultimately recycled back to the crude unit. Operation and maintenance procedures which preclude the need for draining of hydrocarbons to the sewer system should be used. Faster startup and shutdown procedures are being developed which result in less waste being generated at those crucial times.

Recycling to outside service companies is effective for certain oil streams. Some recyclers take used lube oils from vehicles and heavy equipment for re-refining to usable products or inclusion in certain waste fuels. Hydraulic fluids and radiator coolants can be managed on a recycle basis by trading used material for new material.

## 4.7 Solvents

Various solvents are used in maintenance activities within refineries to clean or degrease pumps and machinery. These solvents become contaminated with miscellaneous hydrocarbons as well as solid particles such as sand, grit, and metal. Solvents may contain chlorinated hydrocarbons not suitable for recycling to the refinery slop oil system; the usual management procedure is to recycle solvents off-site by vendor or to reclaim them by installing an on-site distillation system. Please note however, that the recycling of solvent may be a regulated activity.

Some vendors supply fresh solvents and containers for use in machine shops or maintenance garages. The vendors own the solvents and replace old ones with newly distilled material on a routine change out basis.

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An alternative to vendor supplied solvents is an internal system to distill and reclaim solvents. Packaged systems are available in a wide assortment of capacities to handle different types of solvents. These systems may only be economical for large refineries with solvent usages exceeding 1000 gallons per year.

# 4.8 Spent Caustics

Caustic solutions are used in numerous refining processes to absorb and remove contaminants from intermediate and final product streams and to remove hydrogen sulfide from gas streams. Some of these processes result in spent caustics that can be regenerated and recycled within the refinery. Other processes are operated such that the caustic needs to be purged from the system without regeneration.

Caustic treatment to remove hydrogen sulfide and mercaptans from gas and product streams produces a spent sulfitic caustic which must be carefully managed to avoid release of hydrogen sulfide.

Caustic treatment may also be used to remove phenolics, cresylics, and naphthenics (all referred to as phenolics) from refinery naphtha and distillate streams. The quantity and composition of phenolics in the spent caustic depend on the end point of the process stream being treated and the aromatics content of the raw crude. Figure 4.8-1 illustrates how the phenolic content of the treated stream is a function of its boiling point, with the concentration of phenolics increasing as the boiling point rises.

After the absorption capability of caustics is fully utilized, the spent caustics must be removed from the processing system and replaced with fresh materials. Because discharge of spent phenolic caustics to refinery wastewater adds surfactant load that will lead to the production of additional emulsions and sludges, caustics are generally segregated and handled separately.

In some cases, it may be possible to modify the caustic treating process to achieve a substantial reduction in the amount of waste caustic generated. For example, refineries that use nonregenerative scrubbing to treat kerosene streams to meet specifications for jet fuels and home heating oils may find that hydrotreating these hydrocarbon streams is a good alternative to caustic scrubbing (depending on site-specific cost considerations).

## 4.8.1 Recovery and Recycling of Phenols from Caustic

For refineries that have optimized caustic treatment to minimize the amount of caustic used, one of the following practices can be employed to recycle spent caustic to companies that recover phenols either off-site or on-site. Please note however, that recycling may be a regulated activity.

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### 4.8.1.1 Off-Site Recycling

Spent caustic containing phenolics can be sold to chemical recovery companies that specialize in extracting various phenolic isomers that distill at 240 degrees F or higher. These recovered streams are then sold to chemical industries that produce such items as lysol, fertilizers, pesticides, and fibers.

Generally, spent caustic should contain 5 percent or more phenolics in order to warrant recovery in extraction and distillation equipment. A phenolic content between 13 and 14 percent is usually required to recover the cost of transportation to the recovery plant. There is no upper limit on acceptable caustic strength, but sulfide sulfur content should not exceed 0.5 percent by weight.

The phenol recovery process produces a brine effluent that is also sold as a byproduct for subsequent recycling. A final effluent water may require subsequent management. Economics of recovery and recycling is sensitive to environmental regulations placed on the recovery facilities.

#### 4.8.1.2 On-Site Recycling

Phenolic caustics can also be recycled on-site by removing the absorbed hydrocarbons from the spent caustic. Figure 4.8-2 shows a simple sketch of a process that will recover phenolics from spent caustic by pumping to a tank where acid is added to reduce the pH of the caustic to around 3. The phenolics become insoluble and form a separate layer on top of the caustic where they can be skimmed and recycled to a refinery product stream. A basic substance must be added to the remaining caustic to increase its pH to 4 before release back into the refinery wastewater system. It should be noted that difficulties may be encountered when treating the aqueous layer of neutralized phenolic caustic in a biological system. For example, organic overloading and extreme odor problems are possible.

Construction materials for on-site recycling are very expensive owing to the low pH of the process. In addition, because hydrogen sulfide may be released when the pH is reduced, the system must be enclosed, blanketed with an inert gas, and vented to the refinery sour gas system.

### 4.8.2 Recycling Sulfitic Caustic

Spent caustics containing sulfides from treating liquified petroleum gas (LPG), straight-run gasolines, and naphthas generally can be sold or brokered for recovery of sulfides. The economics usually result in a net charge to the refiner, depending on location and on concentration of sulfides and sodium in the spent caustic. Caustics containing sulfides greater than 4 percent by weight with more than 7 percent by weight of sodium are

desirable in the paper and mining industries. Brokers arrange for delivery direct to the user or to their facilities where blends are made before to delivery to the user.

Caustics containing more than 7 percent sodium and less than 1 percent sulfides are desirable to the chemical industry for recovery of sodium.

In all cases, contamination of spent caustics with chlorides or ammonia is highly undesirable because these cause corrosion and air pollution problems when used in recovery processes.

# 4.9 Spent Catalysts

Petroleum refineries use several types of catalysts to increase the quality and quantity of fuels they produce and to assist in treating wastes their process units generate.

Because some catalysts contain noble metals that provide the catalytic activity, they are excellent candidates for recycling. Other catalysts that do not contain valuable metals may be recycled for use as raw materials in the production of products. A European refiner has arranged to use catalyst as a feedstock substitute in brick manufacturing. This section describes the following waste minimization practices for regeneration refinery catalysts for reuse:

- Recycling to metals reclamation
- Recycling to cement
- Recycling to fertilizer plants

Please note, however, that recycling may be a regulated activity.

## 4.9.1 Recycling to Metals Reclamation

Several organizations purchase spent catalysts from refineries to recover metals or regenerate the catalysts for reuse. The activity of the regenerated catalyst may not be as good as needed for its original service, but it may be suitable for another refinery that doesn't require such high catalyst activity.

Organizations that regenerate spent catalysts may sometimes sell them to other users. During its life, a catalyst may be used at several different refineries.

Refinery hydrotreating catalysts generally consist of cobalt and molybdenum or nickel and molybdenum on an alumina support; they are typically regenerated after use. Catalytic reforming catalysts contain platinum or other precious metal promoters on an alumina support. These spent catalysts are sent to specialized recovery organizations for metals reclamation.

Refinery hydrocracking catalysts normally consist of palladium on a zeolite support. After several use/regeneration cycles, hydrocracking catalysts are shipped for metal recovery.

# 4.9.2 Recycling to Cement

During the past two years, there has been increased interest in using spent catalyst from fluid catalytic cracking units (FCCU) as a raw material source for cement manufacturing owing to its high silica and alumina content. At the cement plant, the catalyst is unloaded and stored in a separate hopper with a dust collection system; most cement plants use baghouses for storage. Spent catalyst is blended into the cement mixture along with other solids. In some instances, cement companies will either dedicate an existing hopper system to FCCU catalyst or they may need to construct a new storage hopper. Some cement plants require a commitment of a minimum quantity of catalyst from a refinery over six months to a year to justify the cost of new or modified equipment.

One refinery may not produce a sufficient quantity of spent catalyst to justify the new equipment, but refineries in the same regional area should consider working together to provide the amount necessary to secure a recycling contract with a local cement company.

# 4.10 Spent Clay

Clay filters are utilized in refineries to filter hydrocarbon streams to meet product specifications. Typically, these filters operate on diesel or jet fuel to trap moisture and small particles or to improve color specifications. When the clay material must be replaced, it will often contain significant amounts of entrained hydrocarbons.

Some refineries have been successful at backwashing the clay with water or steam to reduce the hydrocarbon content to acceptable levels so that the clay can be handled as nonhazardous waste. During a backwash period of up to three days, oil is floated off and recovered. One refinery reports that the useful life of the clay can be extended significantly, thus reducing the amount of spent clay produced.

The type of clay employed is important in determining whether water washing will create an unmanageable mud problem. Pelletized treating clay usually can withstand the water wash without forming mud, while pulverized clay will tend to create mud waste. Smallscale trial runs and consultations with the process vendor are recommended to determine the suitability of clay backwashing before implementing this method on a full-scale basis.

# 4.11 Sandblast Media

Proper maintenance of many process units, tanks, and pipes requires painting. Harsh operating conditions and environments can necessitate more frequent painting. The

typical procedure at most facilities is to sandblast the old paint or coating prior to applying a new one. The mixture of spent blast sand and paint chips must be disposed.

If not managed correctly, spent sandblast abrasive can be washed into the sewer system, producing more oil/water separator sludge. Usually, spent blast sand is disposed of as a solid waste in a landfill.

Use of alternative blast media wherever possible reduces the volume and toxicity of material needing disposal. For example, sodium bicarbonate granules, which are nonhazardous and readily soluble in water, can be used in some sandblasting situations. Graded-rock salt, which is nonhazardous and readily soluble, also often can be used successfully.

In general, the primary approaches for reducing the amount of used blast sand are:

- Reduce the amount and/or toxicity of blast media by using less hazardous or alternative media.
- Reduce the amount of used blast media that must be disposed by recycling it.

Examples of methodologies representative of these approaches are discussed more fully below.

## 4.11.1 Abrasive Blast Media

The U.S. Navy has developed and is using another media for paint removal. This material, called Abrasive Blast Media (ABM), comprises a highly specified copper slag that is less toxic than silica sands, but similarly effective for paint removal. The contaminants in ABM (MIL-A-222C2A) are below California's total toxic limit concentration (TTLC) and soluble toxic limit concentration (STLC).

ABM may be used in shipyards and the spent material can be managed as a nonhazardous waste. ABM requires no specialized operating equipment. Because the material is less toxic than sand, little safety control equipment will be needed and disposal costs will generally be lower than for sand.

## 4.11.2 Copper Slag Abrasive with Recycling

As an alternative to sand, copper slag may be used as an abrasive to remove paint and/or coatings. The copper slag can be applied via most traditional sand blasting equipment.

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Copper slag is advantageous because it is heavier than most coatings and, therefore, may be separated and recycled. A mixture of spent copper slag abrasives and paint chips is fed into cyclones. The density differential between the two streams promotes separation. The fines and paint chips are segregated and disposed as a waste because of the metal concentration. Approximately 94 percent of the spent copper slag can be recovered and reutilized for blasting.

### 4.11.3 Alumina Oxide Abrasive with Recycling

Alumina oxide can be used as an effective alternative to blast sand. Alumina oxide is a synthetic product that does not contain the same concentrations of metals as copper slag or sand. The material can be used in traditional sand blasting equipment and it can be recycled through a process of grading, classifying, and cleaning. Vendors will normally build and install the recycling equipment, at their expense, on the customer's facilities. In return, the customer agrees to purchase the abrasive material at a specified price.

## 4.12 HF Sludge Media

Hydrofluoric acid drained from vessel and pump drains in a hydrofluoric alkylation unit is collected through a sealed gravity sewer system into a sump. Typically, the acid is first neutralized with caustic to form NaF and then contacted in a sump with lime to form calcium fluoride which will precipitate. The sludge is periodically removed and deposited in a landfill.

## 4.12.1 Neutralization and Filtration

Sludge volume can be reduced substantially by filtration. Filtration tests have shown the material to be readily filterable using pressure filters such as those described in Section 4.1.4.2. The sludge does not have to be preconditioned as does oily sludge. The excess lime used in neutralization provides the body conditioning that is needed.

The sludge itself may be 30 to 35 percent solids. Filtration will produce a cake containing 40 to 45 percent solids, thereby reducing the mass for disposal by 40 to 55 percent.

The volume of sludge from a refinery probably would not justify a permanent filter installation. Arrangements can be made with service organizations to bring in a mobile filtration unit periodically to process accumulated sludge.

## 4.12.2 Production of Fluorspar

If lime neutralization is employed, the calcium fluoride slurry can be converted to fluorspar, which can be sold to the steel and glass industries as a fluxing agent.

# 4.13 Cooling Tower Blowdown

Cooling towers transfer waste heat from refinery operations to the atmosphere. Traditional units found at refineries employ recirculating water systems where waste heat is absorbed into water and released to the atmosphere at temperatures above the ambient wet bulb temperature. A simplified sketch of an industrial cooling tower is shown in Figure 4.13-1.

The bulk of the heat is removed by evaporation of a portion of the water as it passes countercurrent to air within the packing portion of the tower. Normal operating conditions (1000 BTU per pound of water vaporized) evaporate approximately 1.2 percent of the circulating water being evaporated per 10 degrees F temperature drop across the cooling tower.

Evaporation of the water results in an increased concentration of dissolved salts in the remaining cooled water. These salts can build up to the point where they saturate the solution and precipitate onto the cooling system equipment. It is normal procedure to control the dissolved solids concentration by purging or blowing down a portion of the recirculating water. Sections 4.13.1 and 4.13.2 describe techniques for minimizing the quantity and toxicity of cooling tower blowdown.

### 4.13.1 Minimizing the Quantity of Cooling Tower Blowdown

Solids deposition within the cooling system reduces effective heat transfer and creates sludge that must be disposed. Cooling water systems are typically monitored for calcium sulfate, carbonate and silica deposits. Biological contaminants can also be present because warm, highly oxygenated waters are ideal growth sites for naturally occurring organisms. Cooling water blowdown sludge is a "primary sludge" and it is best to try to prevent formation of the sludge when possible.

The most common scale in industrial cooling systems consists of calcium carbonates, the products of naturally occurring calcium hardness and alkalinity. Noncarbonate scale appears when the solubility products of calcium sulfate and silica are exceeded in the cooling waters. Concentrations of calcium sulfate and silica greater than 1500 and 50 mg/l, respectively, are maintained in the recirculating system by adjusting blowdown rates and monitoring makeup water quality in order to reduce the probability of scaling.

It is important to recognize that cooling tower blowdown should be addressed on a site specific basis after careful water quality analysis. Other publications (e.g., API's 1977 publication on Water Reuse) discuss reducing refinery wastewater in more detail. Briefly, techniques for minimizing the quantity of blowdown include: makeup water quality adjustment (by either source control or water treatment) and recirculating water treatment.

If the concentration of dissolved solids in the cooling water is kept low, more water (cycles of concentration) can be run through the cooling tower. Total dissolved solids (TDS) can be removed from the cooling water makeup stream by: cold lime softening, reverse osmosis, or electrodialysis. These well known technologies are frequently employed to improve the quality of fresh water makeup rather than for blowdown minimization.

Makeup treatment systems can frequently reduce the quantity of blowdown significantly. A simplified calculation is presented in Table 4-1 to illustrate potential of blowdown minimization. If treatment system cycles of concentration can increase from 3 to 10, the blowdown rate for a 50,000 gpm recirculating cooling tower will decrease from 850 gpm to 150 gpm. Fresh water makeup is similarly reduced from 2700 gpm to 2000 gpm. Thus, makeup water treatment can minimize waste production while conserving refinery cooling water makeup.

An alternative to treatment of the full cooling tower makeup is a judicious selection of the source of this makeup. Most refineries have been sited for their easy access to crude feedstocks or surface water for feed and product transportation. Refinery locations often have several potential sources of makeup, from local surface water, groundwater, possibly some higher quality blowdowns such as high pressure boilers on site, and possibly some water reuse options from local industry.

Careful review and selection of makeup source(s) may enable a cooling system to run at higher cycles of concentration. Parameters of concern include the concentrations of calcium, sulfate, and silica and the pH of the stream. Makeup sources are less likely than full-flow makeup treatment to have significant waste minimization impacts, but the capital costs for the former are also much less than those for the latter.

Table 4-1 Impact of Makeup Treatment on Cooling Tower Blowdown Rate		
	Untreated makeup	Treated makeup
Recirculating Water Flow Rate, gpm	50,000	50,000
Temperature Drop, °F	30	30
Cycles of Concentration	3	10
Makeup Rate, gpm	2,700	2,000
Blowdown Rate, gpm	850	150

## 4.13.2 Minimizing the Toxicity of Cooling Tower Blowdown

Cooling tower systems are treated to control deposition by the following means:

- Corrosion inhibition
- Biological growth control
- pH adjustment

Corrosion inhibitors pose the most significant toxicity issue because the most effective compound for this purpose, hexavalent chromium, is a hazardous constituent. Because chromate removal processes have operating problems and other difficulties, many refineries use non chrome technology. With close monitoring, performance of nonchrome inhibitors can approach that of chromate-based compounds. Selection of inhibitor type is a function of water quality, system metallurgy, and pH controls.

When hexavalent chromium is used, effluent treatment can be performed in a two-stage chemical reaction of the blowdown stream. The well-known chromate precipitation process produces a sludge that requires additional management for disposal. Waste flows are not altered but the chromate concentration is reduced from 20-50 ppm to less than 5 ppm in the unit effluent which should meet final effluent limitations for most refineries. Another technology for chromate recovery is ion exchange.

Biological growth control is commonly managed by chlorine vaporization into the cooling system. Some operators are utilizing other biocides or bromine donors as alternatives to chlorination.

Adjustment of pH is used to control carbonate scaling and other constituent solubility concerns. Control of pH is commonly achieved by the addition of sulfuric acid. Because acceptable pH control ranges in the recirculating water system, and thus in the blowdown, and within normal discharge limits, pH control has little impact on toxicity.

# 4.14 Miscellaneous Wastewater System Wastes

Much refinery waste is generated in the wastewater treating system. Biosolids are products of biotreatment methods used to remove organics from the wastewater stream. Chemical sludges can occur in the wastewater system when flocculent-producing chemicals are utilized. Even flow of clean water in the system can absorb organics from floating oil layers and lead to more organic loading and additional biosolids. The following sections discuss some alternatives that can reduce the amount of wastes generated in the wastewater system.

### 4.14.1 Replace Phenol Extraction

Some refiners utilize a phenol extraction process to remove wax compounds from lube oil feedstocks. This process usually involves numerous extraction machines and extensive distillation equipment to recover and reuse the phenolic material, which is very expensive and can cause high organic loading if spilled to the sewer system.

Elaborate valving and piping in the phenol extraction system creates a high potential for drips and leaks that tend to overload the wastewater system by producing a high organic loading. As a result, more biosolids are generated.

Several refiners have converted their existing extraction systems to replace phenol with less costly and less hazardous materials.

## 4.14.2 Changing Coagulation Chemical

In most refinery wastewater treatment systems, after primary gravity separation to remove oil and solids from wastewater in an oil/water separator, secondary physical separation takes place. This process normally removes additional oil and suspended solids before the wastewater is treated in a biological oxidation system. In U.S. refineries, the most frequently employed secondary treatment method is Dissolved Air Flotation (DAF); others include chemical flocculation with gravity settling, media filtration, and induced air flotation. Each of these approaches usually includes use of chemical coagulation and flocculation.

Coagulation is a process in which chemicals are added to wastewater to neutralize surface charges in the wastewater. Those charges cause suspended particles to repel each other, keeping the particles apart. In wastewater, the finely divided particles are predominantly negatively charged. Once these charges are neutralized or destabilized, the particles can be brought into contact with each other, so that they coagulate.

Coagulation technology has been used in raw water treatment to remove suspended material before providing water for domestic or industrial uses. Chemical anticoagulants include aluminum or iron salts such as aluminum sulfate [ $AI_2(SO_4)_3$ .18O], and ferric sulfate [ $FeCI_3x4 H_2O$ ]). Reactions with sodium bicarbonate in the water produce  $AI(OH)_3$  and  $Fe(OH)_3$  flocs.

Polyelectrolytes (water-soluble organic polymers), serve as coagulant aids to bridge across the small floc particles and produce larger, stronger particles that will settle rapidly without breaking up.

Successful operation of DAF units has been achieved by replacing alum or iron salts with all-organic systems. In a typical case, a cationic polymer is used to neutralize the particle surface charge and bring about the formation of pinpoint floc. An anionic polymer is then

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used for agglomeration. With such a system, DAF float volumes have been reduced to 0.1 to 0.2 percent of feed volume, depending on wastewater quality.

### 4.14.3 Stormwater Diversion and Reuse

Many refineries have areas that collect stormwater which is free of oil and which contains very low natural contamination. Such areas include streets, parking lots, and certain tank farm areas that are segregated and often drain directly to storm sewers without treatment as long as the effluent permit conditions are satisfied. Use of stormwater as cooling tower makeup may be feasible in some situations, but there are several factors which would need careful consideration.

Asphalt emulsions require water to form oil-in-water emulsions. Stormwater is collected in diversion systems and pumped to the emulsion makeup water tank. The use of fresh water is discontinued as long as stormwater is available. Certain care is needed to filter out solids and trash before the water is reused.

Most stormwater collected from relatively clean areas will be low in hardness and dissolved solids and can be pumped to cooling tower makeup in lieu of fresh water. Trace amounts of oil should not present difficulty if care is taken to blend stormwater at a low rate. Because of the low hardness of stormwater, facilities for softening cooling tower makeup can be bypassed to avoid that treatment cost and reduce the amount of softening wastes that must be handled and disposed.



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# Refining Waste Minimization Practices Case Study 4-1: Street Sweeper to Reduce Oily Sludges

#### Introduction

A large refinery on the Gulf Coast was experiencing accumulation of sludges in the API separation system in excess of 15,000 tons per year (tpy). Since the annual rainfall was typically high, it was believed that dust accumulations on the paved streets were contributing significantly to the separator sludge during rainstorms. After the dust reached the sewer system, emulsions and sludges were formed with the solids, oil, and water in the system. This combination effect led to settled sludge that should be removed and disposed.

Laboratory data indicated that this sludge was 6% oil, 17% solids, and 77% water and that it contained significant amounts of benzene, ethylbenzene, and toluene, but fairly low concentrations of TC metals.

### **Description of Waste Minimization Practice**

In an effort to reduce dust deposits in the sewer system, a trial run was made using street sweepers to vacuum up the dust. One sweeper provided by a local industrial sweeping company was used concurrently with a company-owned sweeper over the 120-day trail period.

#### Effectiveness

During the four-month case study, approximately 510 tons of dry solids were collected and prevented from entering the sewer. This rate of collection extrapolates to slightly over 1500 tons per year. Assuming that typical API separator sludge contains 17% solids, the sweeper program has the potential to reduce overall sludge production by about 8800 tons per year or about 50%. The long-range effectiveness of this program appears to be good.

#### Costs

The contract sweeper was provided and operated for \$560 per day. The companyprovided sweeper cost \$85,000. Manpower, maintenance, and utility costs are not known.

# Refining Waste Minimization Practices Case Study 4-2: Reuse of FCC Fines

#### Introduction

Catalyst fines from a Fluid Catalytic Conversion Unit (FCCU) are costly to dispose in some states. Instead of mixing the fines with water to form a slurry for disposal, one major West Coast refinery is shipping the fines to a cement producer who reuses the material to produce cement. Cement manufacturers can use the FCC fines as an effective substitute for bauxite because the fines consist largely of alumina and silica. Alumina is an essential ingredient in the production of cement.

#### **Description of Waste Minimization Practice**

In order to recycle FCC fines, the refinery had to make certain that the fines were of acceptable quality to the cement manufacturer. Testing of the FCC fines was critical on both counts. The cement manufacturer would not accept the fines unless the alumina concentration of the fines was at least 45%. Testing also indicated that the concentration of trace metals was less than 1%, so that clinkering would not be hindered. The refinery also had to ensure that the material was dry and free-flowing so that it could be transported pneumatically.

When the spent FCC fines are recycled, they are not legally classified as a waste. Additionally, the refinery inspected the trucking and handling of the spent FCC fines at the cement manufacturer to determine if there were any downstream liabilities in the proposed approach. A number of potential recyclers were eliminated because of apparent industrial health and safety deficiencies. The refinery contracted with an experienced hauler to transport the FCC fines to the cement manufacturer.

#### Effectiveness

Recycling eliminated all of the disposal fees and taxes previously associated with landfilling the spent FCC fines. Based on a FCC fines generation rate of 2200 tpy, disposal fees were reduced by \$242,000 annually.

# Costs

Additional analytical data were needed to quantify the composition of the FCC fines. The refinery also expended considerable time and effort to identify a qualified trucking company and cement manufacturer. After these costs were incurred, the refinery's only obligation was trucking the material. Cost of trucking the FCC fines to the cement manufacturer was on the same order of magnitude as the cost of trucking the waste to a disposal facility--approximately \$30/ton.

# **Refining Waste Minimization Practices Case Study 4-3: Alternative Sandblast Media and Recycle**

### Introduction

Sandblasting is a common means of preparing tanks, process units, and piping prior to painting or applying other coatings. Normally, after the sand is used, it is disposed because it is contaminated by paint that contains hazardous components or which has been pulverized to such a degree that recycling is not feasible. To reduce acquisition and disposal cost of the blast sand, one major refinery employed a contractor to supply and recycle an alternative blast medium, aluminum oxide.

### **Description of Waste Minimization Practice**

Sand traditionally used in blast equipment was replaced by aluminum oxide. Aluminum oxide was selected as the blast medium because it offered three advantages over sand:

- Aluminum oxide is more resilient to degradation.
- The chemical composition and particle size distribution after blasting poses a lower hazard risk than sand.
- Aluminum oxide is denser and more resilient, making recycling viable.

The aluminum oxide is used in the same blast equipment as before. After blasting, the aluminum oxide is collected and processed through an on-site recycle plant. The recycle plant is essentially a three-step process of grading. A cyclone is used to separate reusable blast medium from paint and fines. The paint and fines are captured in a baghouse and disposed in a nonhazardous landfill. Recovered blast medium is airwashed and blended with new material to bring it up to specification.

#### Effectiveness

The new process has reduced the amount of blast medium that must be disposed of by 90%. Furthermore, because the blast medium does not contain hazardous concentrations of metals, the spent aluminum oxide can be disposed of as a nonhazardous waste, which further reduces disposal costs. Instead of disposing of approximately 3100 tons per year (tpy) of hazardous spent blast sand, the refinery is only disposing of 310 tpy of nonhazardous aluminum oxide.

## Costs

The capital cost for this recycle plant was approximately 1.5 million dollars. This cost, however, was borne by the vendor. The refinery agreed to purchase enough of the aluminum oxide (new and recycled) at \$200/ton to justify the vendor's capital expenditure. The refinery reports that the fuel oil consumption for the recycle plant is approximately 11,000 gallons per year and estimates maintenance expenses at \$60,000 per year.

# Refining Waste Minimization Practices Case Study 4-4: Deoiling of Desalter Effluent

## Introduction

A West Coast refiner has a desalter producing 13,675 tons per year (tpy) of oily water containing approximately 6.3 weight percent oil and 0.1 weight percent solids which would ordinarily be discharged to the refinery wastewater system. If allowed in the wastewater system, the oily water forms sludges and emulsions that would have to be removed and disposed.

### **Description of Waste Minimization Practice**

As part of original construction, the refiner installed an oily water treatment unit downstream of the desalter. The purpose of the unit is to remove insoluble oil from desalter wash water containing emulsified oil. Figure C-4-4 is a simplified flow diagram showing a typical system.

The oily water stream from the desalter is contacted with 1647 tpy of naphtha and a surfactant chemical. The water-oil-solvent stream is mixed in an in-line, low-shear mixer and proceeds to the main separator vessel, where an electrostatic field is established to maintain a sharp hydrocarbon/water interface and to assist in the separation process. The separation occurs because of density differences between the two phases.

The distillate solvent containing oil extracted from the water exits the top of the main separator and is sent to crude oil storage. Oil-free water (12,800 tpy) is discharged from the bottom of the vessel and proceeds to the refinery disposal system.

#### Effectiveness

The oily water treatment unit removes approximately 862 tpy of oil. Treated wastewater typically contains 100 to 500 ppm oil and grease and 25 to 200 ppm solids. Assuming an API separator sludge composition of 70% water, 20% oil, and 10% solids, sludge generation is reduced by at least 122.4 tpy. At a nominal \$200/ton disposal cost, annual disposal cost savings would be \$24,500/year. The user reported initial difficulties with the mixer supplied with the treatment unit, and installed an in-line mixer to replace the original equipment. Aside from this modification, the unit has operated for nine years with very little maintenance. The long-range effectiveness of this system appears to be good.

## Costs

The capital cost of the oily water treatment unit is approximately \$60,000. Naphtha use amounts to 525,600 gallons per year and Naphtha is recovered. Approximately 730 gallons per year of surfactant chemicals are used (1979 average cost for surfactant chemical was \$10.93/gallon). Electrical power consumption for this unit is not known.



# **Refining Waste Minimization Practices Case Study 4-5: Screening of Solids from Exchanger Cleaning**

## Introduction

A midwestern refinery hydroblasts solid residue from heat exchangers. The solid residue entered the sewer along with the blasting water and produced additional oily sludge in the wastewater system.

# **Description of Waste Minimization Practice**

The heat exchanger hydroblasting operation generates 50 tons per year (tpy) of solids, 451 tpy of water, and 25 tpy of oil. Screens are placed in the oily water sewer at the location where the hydroblasting operation is performed. The screens collect the solid material but allow the water and oil to pass to the wastewater treating system. After the hydroblasting process is complete, the screens are removed from the sewer and the accumulated solids are disposed.

#### Effectiveness

The refinery reports that 50 tpy of solids are collected dry enough to go to disposal directly without further dewatering. If the same solids had gone to the API separator, they would have been removed with large volumes of water which would have required an additional dewatering step.

#### Costs

The screens are included as part of the hydroblasting contractor's scope of work. The incremental cost for the screens is not known.

# Refining Waste Minimization Practices Case Study 4-6: Spent Jet Fuel Treater Clay Deoiling

#### Introduction

The final step in the production of jet fuel is typically filtration through clay towers. The clay retains impurities in the fuel remaining from prior refinery steps. Spent treater clay with entrained jet fuel must be disposed in a hazardous landfill.

A West Coast refinery generates approximately 1100 tons per year of spent filter clay, which contains approximately 30% jet fuel.

#### **Description of Waste Minimization Practice**

The waste minimization practice used at this site consists of spent clay washing. After the jet treater clay is exhausted, water is injected into the vessel containing the spent clay continuously for three days to flush out the entrapped jet fuel. The wash water is sent to a tank where the two immiscible phases separate. The recovered jet fuel is then recycled. The stripped solid clay has been rendered nonhazardous, and it can be dumped into roll off bins and sent to a nonhazardous landfill.

#### Effectiveness

Water washing entrapped jet fuel from spent treater clay converts a hazardous waste into a nonhazardous waste, greatly decreasing disposal costs. Approximately 2,000 barrels per year of jet fuel is recovered and recycled.

#### Costs

Capital costs are insignificant if existing piping and tankage are used. Operating costs are minor and consist of the cost of the wash water and operator hours.

# Refining Waste Minimization Practices Case Study 4-7: Sludge Coking

## Introduction

A large integrated refinery on the East Coast was disposing of oily sludge at an on-site land farm. Sludge was generated at a rate of 200 BPD and consisted of DAF float, API sludge, slop oil emulsion solids, biosludge, and tank bottoms. Composition of the sludges was 5% oil, 30% solids, and 65% water.

### **Description of Waste Minimization Practice**

In 1975, the refinery modified its delayed coking unit, which produced 2200 TPD of fuel grade petroleum coke, to inject the above oily sludge and biosludge. In the new process, the sludge is injected into the quench water during the quench cycle of the delayed coking process. The attached Figure C-4-7 depicts the flow scheme.

The volatiles in the sludges are flashed overhead and recovered in the blowdown system. Heavy hydrocarbons and solids are incorporated in the coke matrix and become part of the coke product, which is sold for its fuel value.

#### Effectiveness

Land disposal of the waste was eliminated, and the hydrocarbons in the waste were recycled to produce fuel and coke products. The average ash content of the product coke increased slightly from 0.20 wt% to 0.25 wt%.

# Costs

In 1975, the approximate capital cost of the system was \$150,000. Today's cost would be \$200,000 to \$300,000. There are no incremental manpower requirements because current staff operators can run the system. Utility requirements are estimated at \$90,000 per year including in-plant transportation. Overall operating costs are estimated at \$2 per barrel of sludge including capital charges. Off-site, hazardous waste disposal would cost on the order of \$40 per barrel.



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# Refining Waste Minimization Practices Case Study 4-8: Chemical Recovery Process

#### Introduction

A U.S. refinery operated a Stretford unit as a tail gas treatment facility downstream of a Claus sulfur recovery unit. The capacity of the Stretford unit was approximately 5 long tons/day. While a Stretford process is intended to convert hydrogen sulfide in the gas being treated to elemental sulfur, a small percentage of the hydrogen sulfide is converted into fixed sulfur salts such as thiosulfate and sulfate.

The buildup of these salts can be tolerated up to certain levels. As the salt concentration increases, however, active solution must be dumped or purged to control the buildup. This particular refinery periodically dumped solution and sent it to off-site disposal. The possibility of the off-site disposal being curtailed and the costs of disposal and chemical make-up prompted the refinery to investigate alternatives.

#### **Description of Waste Minimization Practice**

A small Stretford Chemical Recovery Process (SCRP) unit was installed. A purge stream was pulled off the discharge of the circulating Stretford solution pumps. The purge was directed to a small solution storage tank where sulfur particles in the solution were allowed to settle. Solution from the tank was pumped to the SCRP unit for processing to recover the active chemicals in the solution. The treated solution was discharged to the refinery wastewater system, and the recovered chemicals were returned to the Stretford unit in the form of a regeneration stream.

This SCRP unit was undersized relative to the capacity of the Stretford unit. The SCRP unit could process approximately 700 gal/day purge, whereas design material balance calculations indicated that a 1600 gal/day unit was required to match the capacity of the Stretford unit.

#### Effectiveness

During the three years prior to installing the SCRP unit, solution inventory was partially dumped and disposed every 2½ months. After the unit was installed, the frequency of dumping was reduced to once per year. During the three years before implementing chemical recovery, the quantity of solution disposed averaged 225,000 gal/year. SCRP reduced disposal to an average of 25,000 gal/year. A full-size unit would have eliminated solution dumping entirely.

#### Costs

Solution disposal at the time cost about 30 cents/gal. Consequently, \$60,000 per year in disposal costs were saved through use of the process. In addition, chemical make-up cost savings were approximately \$120,000 per year.

A new, full-size unit was designed for this application. It was estimated to cost \$750,000. The disposal and chemical make-up cost savings after subtracting operating and maintenance costs resulted in positive cash flows that gave the project a 15% discounted cash flow rate-of-return.

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# 5 Marketing Waste Minimization

Marketing facilities are widespread and diverse with varying degrees of complexity. They range from small gasoline-dispensing retail outlets to large, storage and distribution terminals and more complex facilities including manufacturing plants dedicated to grease compounding and oil blending. Depending on the types of activities in the marketing facility, marketing waste streams may need to undergo analysis, especially the TCLP, to determine whether they are subject to hazardous waste disposal requirements.

The "typical" marketing facility is neither complex nor sophisticated. The primary function of the marketing chain is the receipt, storage, mixing and blending, distribution, and ultimate sale of refined products to the consumer. Because of the nature of such functions, the marketing phase produces only relatively small quantities of wastes on an intermittent basis. These wastes encompass oily sludges from sumps, drains and separators; off-specification oils from product blending, laboratory testing, and off-specification products; used oils from normal operations; emulsion-causing cleaners, solvents, detergents, and acids; small quantities of toxic additives; solid waste from auxiliary products including tires, batteries, vehicle parts, and oily rags; contaminated soils from procedures; and potentially contaminated stormwater runoff.

Described below are examples of waste minimization practices, and is by no means exhaustive.

# 5.1 General Procedures for all Marketing Facilities

Prevention of oil releases constitutes the first significant step toward total waste minimization at marketing facilities. Safeguarding against spills and leaks is best handled through good housekeeping, maintenance, and inventory control procedures. No facility should overlook the use of any possible release detection systems or procedures, including the daily use of an inventory control system (See API Publication 1621, "Recommended Practice for Bulk Liquid Stock Control at Retail Outlets" and Bulletin 1623 "Recommended Good Practices for Bulk Liquid - Loss Control in Terminals and Depots").

If a release does occur, prompt recovery of spills and leaked products should be accomplished to prevent the residue from mixing with various facility streams, particularly the uncontaminated stormwater runoff.

Another important factor is to prevent emulsion-forming materials from getting into facilities' wastewater treatment systems. Soaps, detergents, chemicals utilized in plant and automotive cleaning, and acids and cutting oils can form emulsions that defeat the effectiveness of oil-waste separation equipment. Therefore, the isolation and containment of cleaners, chemicals, oils and emulsions formed is suggested.

# 5.2 Classification of Marketing Segment Facilities

While storage, manufacturing, and retail facilities each require individually tailored source contamination prevention procedures, good housekeeping and maintenance should be considered at all outlets. Because of the diversity of operations and the variation in contaminants handled, procedures for minimizing waste will be addressed separately for the following marketing segments:

- Storage and Distribution Facilities These operations conduct no manufacturing; rather, they are engaged strictly in the storage and distribution of light petroleum products.
- Complex Facilities These sites handle a full range of petroleum products including heavy oils. This category includes plants where activities such as ballast receiving, aviation servicing, lube oil blending, or grease compounding are conducted.
- Retail Outlets This segment includes the full range of service facilities that provide finished product and service to the ultimate consumer.

Overlapping of programs across categories will be discussed as appropriate.

# 5.3 Refined Product Storage and Distribution Terminals and Bulk Plants

The petroleum industry maintains about 35,000 bulk plants and terminals for receipt, storage, and distribution of refined products. Distribution terminals receive refined products by pipeline or marine transport while bulk plants, which are normally smaller, receive products by truck and occasionally by rail tank car.

Under normal circumstances, the volume of operational discharge from individual plants is relatively small. Additionally, some contaminants can be successfully recycled, consumed, or safely disposed of if appropriate programs are initiated.

# 5.3.1 Terminal and Bulk Plant Yard Areas

At most terminals, the yard area is surfaced with asphaltic concrete or other impervious material. These areas should be maintained according to best management practices. The areas should be swept routinely. Leaks and spills should be contained and all contaminants released from operating areas should be isolated and treated separately so that stormwater is not contaminated.

# 5.3.1.1 Stormwater Runoff

Stormwater runoff constitutes the principal discharge from marketing terminals. Wet weather discharge of uncontaminated stormwater can range from 200,000 gallons/year at a typical bulk plant to more than 5 million gallons/year at a large terminal. Stormwater discharges may need to be handled in accordance with the appropriate permits issued under the regulations on stormwater discharges.

In order to accomplish the successful isolation of this large volume of uncontaminated stormwater from operational water streams, a complete survey of the product storage and handling areas may need to be conducted. Contaminated aqueous effluent from plant operations may be isolated from stormwater drainage, then treated and discharged in accordance with appropriate permits or transferred to another location for appropriate treatment and discharge. Alternatively, where complete isolation of petroleum streams can be accomplished, effective recycling or reuse on-site may be used.

The dry weather flow from terminals is composed mainly of truck wash water, sanitary waste, boiler blowdown, waste from maintenance bays (such as antifreeze, used oil, solvents and various cleaners, degreasers, and aluminum truck acidic brighteners) ballast water off-loaded from vessels, and discharges resulting from floor, equipment, and loading rack slab washing. Specific areas where there is potential for product and/or contaminant release and typical corrective measures to prevent this discharge are discussed in the following sections.

# 5.3.1.2 Filter Separators

During normal operation, correctly functioning filter separators should not release any contaminants to the environment. Because these filters treat oils such as kerosene, any spillage during changing or recharging of the filter media will release persistent products which, if not immediately cleaned up, can contaminate rainwater in the future. During maintenance and filter removal, absorbent work pads can prevent oils from infiltrating the ground.

# 5.3.1.3 Air Eliminators

Properly installed air eliminators will minimize the release of contaminants. Efficient collection, containment, and removal of water and oil particles expelled during normal air eliminator operation will also help prevent any release. In most cases, collection of waste product can be accomplished by piping both the water and air release outlets directly to a collection tank. Periodic routine checks must be made to ensure that the collection tank does not overflow. When there is a possibility of overfill of the collection tank following malfunction of the separator, waste products can be directed to a containment area. Alternatively, an automatic alarm can be installed to alert plant personnel of the need to drain the system. Oil removed from the collection tank can be returned to storage while

the small quantity of contaminated water and solids can be readily disposed of with other treated plant effluent.

# 5.3.1.4 Loading Racks

Truck loading operations at terminals and bulk plants can provide a significant source of oil that can contaminate rainwater runoff. A means of waste minimization in the loading rack area is to minimize the rainfall coming in contact with this oil. Roof canopies over the loading slab are an effective way to minimize contamination because they enable stormwater falling on the roof to be routed through drains to uncontaminated areas. In addition, it may be useful to extend existing roof canopies to cover the entire curbed area. Rainwater contamination also can be prevented by diverting the rainwater away from the loading rack by raising the loading rack slab and sloping the yard pavement down and away from the slab. The curbed areas in loading rack areas also should be evaluated. The loading rack area may be able to be decreased, thus minimizing the rainfall in the area.

To prevent the undesirable release of oil, consideration should be given to fail-safe design features. Among the features to be evaluated are an interlock warning light or physical barrier system to prevent vehicle departure before complete disconnect of the transfer line. Also, prior to movement of any tank truck or tank car, the lowermost drain and all outlets should be closely examined for leakage to prevent product spillage while in transit.

Any drippage and spills at the loading rack can be contained and/or collected with perimeter curbing, strip drains, or strategically located sumps. Systems can be installed directly in the loading area to collect any product spilled or released. The discharge from the containment area also can be routed to a retention or treatment facility. Where dedicated collection tanks are installed to receive only water and compatible hydrocarbons, the collected and separated product can be returned to storage for reuse. It is useful, however, to ensure that solvents and cleaners are not introduced into the system. Normal safeguards include regular gauging of the collection tank or automatic high level alarms. Also, the gravity flow should be designed to ensure complete drainage into the collection vessel to prevent the strip drains, traps, or sumps from retaining light oils that may create a fire hazard.

# 5.3.1.5 Product Pump-off and/or Truck Unloading

Because of the possibility of spills and drippage while disconnecting hoses, areas surrounding truck unloading connections are frequently curbed and the area is provided with an impervious surface. An alternative method is to install drip pans under the hose connection position. These pans can be drained directly to collection tanks to facilitate later pumping back to tank storage for reuse. To prevent water from mixing with the recovered product, covers are normally placed over the drip pans when they are not being used.

# 5.3.1.6 Tank Car Unloading

Stringent operating procedures will tend to reduce product release during tank car loading and unloading. For example, inspection of the drain block and all outlets before moving tank cars and positioning the tank cars so the fill and unloading facilities are over the spill collection facilities can reduce product release. In many tank car unloading facilities, it has been found that drip pans located under the hose connections can satisfactorily recover any spilled products. These drip pans can then be piped to central collection tanks for later recovery and return to storage. To prevent stormwater from entering the system, three-way valves can be designed to close the drainage line and/or divert stormwater away from the area when tank cars are not being unloaded. As with all spill collection tanks, routine gauging or high level alarms should be considered.

# 5.3.1.7 Empty Drum Storage

Most empty drums at marketing facilities have been returned by customers who have used the oils and lubricants formerly contained in the drums. Care should be taken to determine the regulatory status of the empty drums. It is essential that only empty drums be returned to the plant and that residue consist only of lubricating oils. Additionally, it is important that all drum openings be securely capped and that the drums be stacked with tops up. Consideration should be given to use of containment curbs and diversion of runoff from the empty drum rack area to an oil-water separator for treatment. Alternatively, use of canopies or other forms of cover to prevent stormwater from adding to the runoff can be beneficial.

Another strategy is to keep the returned drums to a minimum by selling them with the product or having the customer forward them directly to a reconditioner. Drums that have been used by customers for collection of wastes should be refused. In addition to returned oil drums, some containers at marketing facilities are obtained with purchased chemicals or additives. If the material purchased is hazardous by federal or state regulations, the residues must be handled as specified by those regulations. Purchases from suppliers who recycle their returned drums may be preferred over those from vendors who refuse to take back empty drums. Purchasing procedures that reduce the number of drums requiring disposal are generally preferable.

# 5.3.2 Truck Maintenance Bays

The truck repair bays at marketing plants and terminals generate some wastes that are usually not compatible with other plant effluent streams. In most cases, these wastes (solvents and absorbent used to remove oil and grease as well as various soaps and detergents) will form emulsions that will interfere with efficient oil and water separation. When discharges containing detergents, chemicals, acids or soluble oils may not be compatible with normal facility waste water treatment, wastes from the truck maintenance

bays may be isolated, treated, and disposed of separately. Where it is not feasible to treat these effluents separately, the waste should be recycled or contained and transported to a facility that can handle it acceptably. Specific wastes generated at truck maintenance bays are discussed in detail below along with suggested disposal practices.

# 5.3.2.1 Antifreeze (See also Section 5.5.5)

At marketing terminals and bulk plants, used antifreeze generated in the truck maintenance bays usually amounts to only the few gallons removed during servicing of the coolant system of the facility's truck fleet. Because antifreeze is water-soluble, it may not be compatible with normal plant gravity oil/water separation or some treatment facilities. Pure antifreeze has a relatively high BOD (biological oxygen demand) and may contain toxic additives that could violate receiving water standards if it is allowed to flow untreated from the plant. Ideally, used antifreeze should be collected in containers and taken to an antifreeze recycling facility, if such a facility is readily available in the area. Alternatively, the fleet's coolant systems can be serviced by an outside facility.

# 5.3.2.2 Solvents (See also Section 5.5.6)

Minor volumes of various solvents and chemicals are used at marketing facilities to clean equipment and in the maintenance garage during vehicle repairs.

During use, the solvents become contaminated with dissolved oils and greases and the road dirt that clings to the equipment being cleaned. Packaged units are available to purify dirty solvents via distillation.

Solvent recycling usually offers the most convenient and economical choice. A solvent tank and basin are provided by the recycler. On a regular basis, the recycler will bring in clean solvent and collect dirty solvent, which is returned to the recycler's central location where large-scale solvent distillation and cleaning will be conducted. Please note however that this may be a regulated activity.

# 5.3.2.3 Used Oil (See also Section 5.5.4)

For the normal marketing terminal, used oil is from the delivery truck fleet. Used oil is normally collected then removed by an outside service company who will re-refine or recycle the oil. It may be preferable to engage an outside company to handle the truck oil changes. As a convenience, many such firms will service the vehicles at the terminal and collect and remove all used oil.

# 5.3.2.4 Floor Cleaners (See also Section 5.4.2)

Preventing spills and drips is the first step toward keeping floors clean and minimizing waste generated as a result of cleaning the floors. When drips and spills do occur,

absorbent materials or pads should be employed to collect any grease or oil drippings. Oil drainings should be collected and disposed of through recycle service firms.

The largest volume of waste generated in cleaning floors is typically water. Absorbent used to clean up oil and grease will minimize the use of water. Floor degreasers and cleaners are generally not compatible with plant treatment facilities and should be avoided. Where floor cleaners are essential, water should be kept to a minimum, biodegradable cleaners should be employed, and the residue should be collected for acceptable disposal.

### 5.3.2.5 Truck Washing (See also Section 5.5.3)

Typical truck wash effluent contains elevated levels of oil and grease as well as suspended solids. At locations with automatic truck washers that consist of separate wash and rinse arches, the quantity of water needed for each truck ranges from 100 to 200 gallons.

Actually, the oil and grease level is not a true measure of the oil present in the effluent, because the EPA analytical method measures other organics present, such as the surfactant in the detergent, along with the oil. Because the contaminants in the cleaning water are emulsified by the detergent used, the normal treatment equipment at marketing terminals (oil/water gravity separators, carbon adsorption, etc.) has limited effectiveness for removing the soluble organics in this particular waste stream. It is therefore important to isolate truck wash water from the routine marketing plant effluent. If the untreated discharge cannot be routed to a sanitary sewer, the wash water can be contained and treated with inorganic coagulants (alum, lime, ferric chloride, and ferric sulfate) and/or polyelectrolytes to remove COD (Chemical Oxygen Demand) and suspended solids. Following chemical treatment (coagulation-flocculation), the solids residue is nontoxic and compatible with normal landfill waste so that the liquid may be discharged to a sanitary sewer.

Where isolation from other plant effluent and dedicated treatment is not feasible, alternative methods should be employed to reduce the quantity of waste. At locations with small truck fleets or where the alternate treatment procedures are not acceptable, consideration should be given to the use of outside truck wash facilities. Another option is to install a treatment system to permit reuse of all truck wash water.

#### 5.3.2.6 Aluminum Brighteners

Unpainted truck trailers are periodically treated with an acidic brightener. This aluminum brightener is generally a corrosion-inhibiting acidic cleaner, and the treatment yields lowpH waste water. Where a terminal maintains a sizable fleet of aluminum trailers, provision should be made to discharge the waste from this treatment to the municipal sanitary sewer. Generally, however, for most plants with only a couple of truck trailers,

it is cost effective to send the trucks to an outside service company where this acidic brightener service is conducted on an ongoing basis and treatment of the waste stream is appropriately handled.

# 5.3.3 Tank Basins

In most cases, tank basin levees are constructed of well-compacted earth, reinforced concrete, or waterproofed reinforced concrete block. In areas of porous soil, an inverted dike should be extended either to the lowest recorded water table elevation or to an impervious soil stratum. Alternatively, an impervious barrier should be installed on the surface of the tank basin. The diked area should be designed with a capacity to contain the contents of the largest tank, plus sufficient freeboard to hold any stormwater within its limits.

Because the tank basin is strictly a fail-safe feature designed to prevent large spills from being released, there should be no oil or grease present during normal operations at a well-maintained facility. During equipment maintenance procedures, spills or contaminant releases within the tank basin should be absorbed and removed immediately. All surface stormwater can be gravity routed to a low area within the tank basin where there is a drainage system to release the uncontaminated water. Typical designs will include a sump connected to a pipe drain through the dike with a block valve and a provision for locking. Alternatively, many bulk plants utilize swing-jointed stand pipes which are lowered after a storm and raised immediately following drainage of the dike area.

Stormwater discharges must be handled in accordance with the appropriate permits issued under the regulations for stormwater discharges. To minimize contamination of stormwater, the following are several safeguards that can be employed:

- The dike drain valve is locked closed at all times when not being used.
- Prior to release of stormwater, an inspection is made to ensure compliance with applicable water quality standards.
- Adequate records are maintained for each draining of the tank basin.

In the following sections, some of the specific operations within the tank basin are discussed in detail.

# 5.3.3.1 Tank Water Draining

Preventing water from getting into the tanks is a means of minimizing tank water draws. Tank water bottoms contain not only oil but also alcohols, naphthenic acids, phenols, and

numerous other chemical additives. The discharge is high in COD, BOD, solids, and other compounds and, if released untreated into the tank basin, could contaminate groundwater or a large quantity of stormwater. In order to reduce the volume of water that has to be removed from the tank, the following actions can be taken:

- Water in the product may be minimized as follows:
  - Closely monitor all pipeline receipts to ensure that water is not included with the product tender.
  - Check all barges and tankers for water prior to receipt.
  - Monitor truck and tank cars for water in product being received.
- The entry of stormwater into storage tanks may be minimized through one of the following measures:
  - Construct covered floating roof tanks.
  - Equip open floating roof tanks to prevent water from entering the product (usually by use of internal drains and well-maintained roof pan seals).
  - Retrofit open floating roof tanks with geodesic domes.

After minimizing the amount of water entering the tanks, the remainder which may have to be drained should be treated and disposed of in accordance with appropriate regulations and permits.

# 5.3.3.2 Sample House

At terminals where product samples must be taken during receipt, equipment should be designed to prevent drippage or spillage. Frequently, sample testing is implemented by extending fixed piping from the line taps into a sample house where tests can be made and unneeded product can be returned to a collection vessel or tank. All sample product that does not have to be retained for quality assurance should be returned to storage.

# 5.3.3.3 Additive Injection Facilities

Some additives can pose unique environmental concerns because of their water solubility and/or toxicity. Injection systems should be designed to prevent contaminants from being released within the tank basin. Features used to prevent spillage include a fixed piping system from the additive supply directly to the receiving tank or to the tank's product

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supply line. Where feasible, storage tanks supplied by tank trucks or tank cars are preferable to drum receipts. Locations where spillage may occur, such as the truck delivery connection and drum handling areas, should have containment and collection equipment. Normally, it is preferable to return any contaminated additives to the supplier.

## 5.3.3.4 Tank Cleaning

Before cleaning storage tanks, every reasonable effort should be made to extract all recoverable product and return it to storage. During the cleaning process, the residue remaining after all recoverable refined product has been removed consists of a liquid phase and a solid phase. The liquid is primarily water with a small amount of hydrocarbons that readily float on top of the solids. The oil content of these sludges is generally low (1 or 2%) for sludges removed from light product tankage such as gasoline. Sludges cleaned out of tanks holding viscous or heavier products, such as fuel oils or greases will contain higher oil content (5 to 50%) because a larger amount adheres to the tank walls. Also, these heavier products contain constituents such as waxes and asphalts that tend to form sludges.

Initial efficient recovery of hydrocarbons is necessary to minimize the amount contained in the liquid phase. This liquid phase can then be treated and disposed of in accordance with appropriate regulations.

The solid phase or sludge is a mixture of insoluble deposits wetted with water and hydrocarbons. These sludges are removed from tankage whenever the tank is taken out of service for repairs or modification. Additionally, there are periodic tank cleanings necessary because of the accumulation of bottom deposits. Small quantities of solids in refined products accumulate as sludge in these tanks, but they can normally operate for periods in excess of ten years without need of cleaning.

In addition to minimizing the quantity of waste by employing every reasonable effort to remove as much hydrocarbon as possible, the procedures listed below should be followed:

- Reduce or avoid slurries by minimizing the water used to clean tanks. (Use only enough wash water to remove the bottom sludge.)
- Recycle the cleaning water; it can be routed to gravity separators for removal of hydrocarbons and solids and subsequent reuse.
- Upon removal of solids, extract all liquids (filter presses can be effective). The water removed can then be treated and disposed of in accordance with appropriate regulations.

Many service companies clean tanks and remove sludge. Some companies offer an assortment of portable sludge minimization services that recover oil for recycling and produce a low-volume solid waste for disposal. Typical equipment will include centrifuges and plate and frame filters. (For details on design and capability refer to Section 4.1.4 and 4.1.5.)

The toxicity of the sludges varies depending on the service for which the tank is used. All storage tanks that have been used for leaded petroleum products will contain residual lead of varying concentrations. During the cleaning of leaded gasoline storage tanks, the residue remaining after all removable liquids have been extracted includes insoluble lead oxide deposits in conjunction with normal rust and scale. All tank sludge, when recovered, should be evaluated for hazardous waste toxicity characteristics.

# 5.3.4 Alcohols

Because of the dramatic increase in alcohols added to gasoline, both as an extender and octane improver, there is increasing likelihood of alcohols getting into plant wastewater. It is important that alcohol storage tanks, unloading positions, and pumping units be segregated from petroleum handling facilities where feasible.

To minimize the quantity of waste generated, storm and plant waters should not be mixed with wastes containing alcohols. Where alcohol does get into isolated wastewaters, such as in gasoline tank water drainings, separate treatment may be required. Small quantities should be acceptable for normal biological treatment and disposal in accordance with appropriate regulations.

Generally, the optimum procedure for handling alcohols is to keep alcohol-containing wastewaters to a minimum, isolate these streams, remove free hydrocarbons utilizing gravity treatment, and dispose of the remaining biodegradable waste appropriately.

# 5.3.5 Marine Docks

Waterfront facilities used for the transfer of products to and from marketing terminals generate minimal wastes during normal operation. Any pollutants which do escape, however, pose a direct threat to the receiving waters below. In the following sections, the main sources of marine dock wastes and procedures for their minimization are addressed.

# 5.3.5.1 Dock Product Transfer Areas

To minimize the quantity of wastewaters generated, most terminals utilize drains under all hose connection positions. These drains, used to contain drippage and drainings when hoses are disconnected, can be routed to collection tanks where they are later reinjected back to storage. To facilitate the reuse of this material, separate collection tanks may be used for compatible families of products. Covers, valving, or some other

means should be provided to prevent stormwater from entering the collection system when product transfers are not being conducted.

These collection systems also provide receptacles for any other waste oils, including product samples that are generated on the docks. Also, consideration should be given to hydrostatic testing of hoses with oils that can later be returned to storage through the collection tanks. To prevent generation of contaminated waste, water should not be used for hydrostatic line and/or hose testing.

By isolating all petroleum wastes, the dock surface remains free of any contaminants. Normally, the dock, surfaced with concrete or other impervious material, is curbed to contain any accidental spill during product transfer. Therefore, if a spill occurs, the collected product can be routed back to storage through the hose drippage collection system. After normal product transfers, it should be acceptable to remove scuppers in the dock curbing to permit discharge of clean stormwater directly to the waterway.

### 5.3.5.2 Sanitary Waste

At dock areas, an evaluation should be made as to whether it is necessary to provide sanitary facilities. All tankers, tugs, and barges are equipped with adequate facilities, including necessary collection tanks and/or waste disposal systems. If it is necessary to provide sanitary facilities on the land side dock, it is usually best to have the waste piped directly to the plant sanitary sewer. Alternatively, either a package treatment facility or an adequately sized holding tank should be provided to enable later disposal to sanitary treatment facilities.

#### 5.3.5.3 Ballast Water

Relatively few marketing facilities need to accept ballast water prior to loading vessels. This waste stream characteristically has a high salt content, solids, and free oil. Many times the only practical method of handling ballast water at marketing facilities is through use of a dedicated treatment system, which normally consists of a gravity separator and containment system (frequently a covered storage tank).

Recovered oil can normally be recycled to the plant's heavy oil storage and the water held for later disposal. Reuse may be achieved by return to the next vessel that off-loads to the terminal; it can be used by the vessel's ballast on its return trip.

# 5.3.5.4 Package Storage

To minimize the buildup of contaminated solid waste, packages should be stored on an impervious floor with an overhead cover to prevent stormwater intrusion. When spills or leaks occur, the waste should be cleaned up with absorbent material and managed appropriately.

Floor washing can be carried out by use of automatic scrubbing machines capable of capturing all wash waters, which can later be disposed of through the truck wash system.

# 5.4 Complex Marketing Terminals

Facilities included under this category include large terminals that handle petroleum products ranging from gasoline to heavy oils, major airport fueling facilities, and locations where complex activities, such as lube oil blending or grease compounding, are conducted.

For oil removal, gravity separation is a common method; oil and water separate upon standing because of the difference in their specific gravities. The separation can take place in a tank or a specially designed separator. By controlling the waste streams and isolating contaminants incompatible with gravity separation, a plant can realize the following advantages:

- By operating on gravity flow, a plant is not subject to malfunction by power failure or breakdown of pumping and other mechanical equipment.
- A gravity separation unit can operate effectively unattended for reasonably long periods of time, such as overnight or weekends.
- A gravity separation unit is capable of operating under most winter conditions and with widely varying flows. This advantage can be particularly significant for terminals with flows varying from "0" during dry weather to several thousand gpm following heavy rainfall.
- A gravity separation unit does not require highly skilled operators or sophisticated maintenance.

It should be noted that in some cases, however, wastewater discharges may require additional treatment to meet discharge permit requirements. Additionally, if a facility is managing TC hazardous waste waters, additional requirements may apply.

More sophisticated methods of removing oil are generally not suitable for use at marketing facilities, but some of the alternatives to gravity separation described below may be applicable at certain locations:

# Coalescers:

Coalescers use a medium to capture small globules of oil on the filter surface, enabling them to come in contact with each other and form larger oil globules. The effective increase in oil globule size makes the oil easier to separate.

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Generally, the small oil content in terminal waste streams and the solid material draining off yard areas (road dirt, silt, and sand) causes early plugging, making the coalescers system inoperable.

#### Filtration:

In filtration systems, oil and solids are effectively removed by physical entrapment on the filter medium. In the case of an oil spill, however, filter materials quickly become saturated with oil, and if they are not regenerated, the resulting oily solid-waste disposal problem becomes unmanageable. Some granular media systems can be regenerated by backwashing followed by recovery of oil and solids.

The main disadvantage with filtration systems at marketing facilities results from the extreme variation in flow. During dry weather flow, the system is not operated and storm surges can unload captured oil if the filter has not been cleaned before the rain. Because of this problem, large holding basins are required, and the filtration system provides limited benefit, if any.

#### Air Flotation:

In this process, small air bubbles are introduced which adhere to suspended oil particles and accelerate their rate of rise. Air flotation systems are not normally suitable for terminal use because they cannot readily handle the widely varying flow rates (zero to several hundred gpm) that are encountered. Air flotation also requires significant operator, maintenance, and monitoring attention which is normally not available at marketing facilities. For effective oil removal, chemical additives are generally required with air flotation, which requires technically trained manpower and entails additional operating costs.

#### Coagulation-sedimentation:

In this process, a chemical is added to the water to form an insoluble flocculent (floc) to which the oil particles adhere. This floc then settles to the bottom of a settling tank. Because large quantities of chemicals must be added to cause the oil to sink rather than float, this procedure is not practical for oil removal at marketing facilities. Disposal of the floc presents additional problems.

#### Centrifugation:

This process utilizes centrifugal force in place of gravity to separate substances with different densities. For oil-water separation, centrifuges are useful only for small, high-strength waste streams such as laboratory wash waters. Centrifugation is not practical at complex terminals because of the high stormwater flows and the significant maintenance problems that would be expected. Successful waste minimization practices at complex marketing facilities require good housekeeping, isolation of operations, segregation of noncompatible wastes, consolidation of similar waste streams, and reclamation of oil primarily by oil/water separation. Specific areas where waste minimization should be employed are discussed below.

# 5.4.1 Boiler Blowdown

At marketing terminals, boilers are used for heating heavy oil, lubricant lines, and storage vessels. To minimize waste, systems should be closed with steam condensate recycled back to the boiler. It is frequently necessary, however, to release a small amount of boiler water (.05 to 2 gpm) as continuous blowdown in addition to the sludge blown out of the bottom of the boiler several times each day.

Boiler blowdown waters have a high pH, moderate amount of organics from the treatment chemicals, and high dissolved inorganic solids. Because of these contaminants, boiler blowdown effluent tends to emulsify any oil present in an oil-water separator and may result in discharges high in oil content.

To reduce waste, steam condensate should be collected and recycled back to the boilers. For the balance of the waste stream, if maximum specifications are set for suspended solids or oxygen demand, another treatment besides simple gravity separation would be required. In such cases, the remaining waste should be managed appropriately.

# 5.4.2 Floor Cleaning

Floors in grease and lubricant manufacturing buildings, maintenance garages, and package warehouses must be cleaned periodically to prevent buildup of oils and greases. Intervals between cleaning can be extended through good housekeeping and a maintenance program that minimizes leaks and drips from the manufacturing and packaging operations. Any drippage that cannot be recovered and recycled should be removed immediately with absorbent and disposed of as solid waste.

Automatic floor scrubbers are normally the best tools for periodic cleaning. They can be programmed to dispense a minimum quantity of detergent-water solution, scrub the floor surface, and then vacuum the liquid back into a holding tank on the machine.

Wastes collected on floor scrubbers is low in volume but high (100-300 ppm) in total organic carbon (TOC), owing to detergent, high levels of oil and grease, and varying amounts of suspended solids, depending on the condition of the floor. The dirty wash water is best routed to the truck wash water containment tank for treatment and/or disposal in accordance with appropriate regulations.

# 5.4.3 Used Oil

Spent lubricant and hydraulic fluid wastes are generated from the routine expiration of the usable life of these fluids in machinery, vehicles, and aircraft. In most cases, spent lubricants and hydraulic fluids undergo relatively small changes in their basic composition during usage. Expiration of useful life is largely based on depletion or breakdown of additives, oxidation of hydrocarbons to acidic compounds, and accumulation of metals from wear or from fuel additives. Unlike contaminated fuels, spent lubricants and hydraulic fluids have a predictable rate of production.

All used oils should be collected and recycled or rerefined. Other disposition may subject used oil to hazardous waste regulations. Please note that the regulation of used oil is rapidly changing. Federal, state and local laws and regulations should be consulted.

When recycling or rerefining is not an option, combustion may be an alternative. Despite the presence of lead and other waste metals, spent lubricants may be amenable to direct disposal by combustion. Crankcase lubricants have been burned with residual fuel in boilers at many locations in compliance with EPA regulations.

# 5.4.4 Loading Rack Slab Washing

Periodic cleaning of loading rack pads using a detergent usually requires significant volumes of water. Because loading rack pads are not necessarily washed down on a regular basis, but only as needed, the best method for reducing this waste stream is to eliminate spills and collect drippage in portable containers rather than have it fall on the slab.

At loading rack slabs for lube oil and heavy refined product, more frequent detergent cleaning is necessary, and the resultant wastewater is contaminated with oil and detergent. Because detergent in the wash water tends to emulsify oil in the water, the wash water may be isolated from the loading rack interceptor tank by valving or other means to block off the rack drainage sumps during cleaning operations.

The volume of detergent, oil, and sludge is increased sizably by water used for flushing the surface and for moving the material out to a portable tank for subsequent treatment. This volume increase may justify the use of a service contractor to reduce the volume by centrifugation or filtration. Alternatively, at large manufacturing plants, it may be costeffective to install a site treatment facility for the various high-strength wastes isolated and collected during washing of loading racks.

# 5.4.5 Sludges from Separator and Sumps

Typical marketing facilities have smaller oil-water separator systems than refineries and usually do not continuously remove and process separator sludges. Instead, these

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separators are shut down on a scheduled basis to remove sludges, which are comprised of oil (5 to 25%), solids (20 to 30%), and water (20 to 80%). The type of oil will be dependent on the various products handled at the facility and the extent of unmanaged drips to the sewer system. The solids in the separator generally come from the soil washed into the system. Solids can also be generated and deposited in the separator via wash down of occasional spills and from chemical interactions that cause precipitates to form in the drainage system. The water content of these sludges is increased when water hoses are used to slurry the sludges for removal by vacuum truck.

To minimize this residual, a service company is often used to recover oil and remove the water from the sludge. The same type of service company as is used for tank bottoms can be employed to centrifuge or filter the sludge to reduce its volume. Recovered oil is sent to be recycled, and the water removed is returned to the oil/water separator or discharged in accordance with appropriate regulations. Separator cleaning may be scheduled to coincide with tank cleaning to reduce treatment costs.

## 5.4.6 Slop Oil and Commingled Product

To accomplish effective waste minimization together with cost benefit maximization, an overall evaluation should be made of a facility's waste streams to determine which petroleum products should be segregated for effective recovery and/or disposal.

Some refined products, such as jet fuel, are highly susceptible to contamination by water, grit, and -- to a lesser extent -- bacterial growth.

In practically all cases, commingled product or slop oil can be blended back into refined storage tanks. Normally these oils are collected in segregated storage until they are blended back into heavy oil (#6), heating oil (#2), or motor gasoline in quantities usually less than ½ of 1%. Sources of slop oil include oil separators, laboratory and product sample wastes, drip pans, spill containment, and line purging and testing.

## 5.4.7 Lube and Grease Manufacturing

Some marketing terminals operate lube oil or grease blending and packaging facilities. These operations can be either batch or continuous systems, which are usually operated to achieve a designated volume of product to meet market demand. Whenever the blending schedule requires a change in product, the system is flushed with rinse oil and sometimes washed with water and detergents. This process produces waste oils, grease, and wastewater.

To minimize these wastes, the schedule of operations may be reviewed to determine if the residual oil in the system is compatible with the next scheduled product. In some cases, the next scheduled product can be made without rinsing or washing the system.

Another way to minimize waste generated between blends is to produce more of a given product during the operating run and then store it for a longer time, thereby reducing the amount of rinse and waste. Issues to evaluate in order to increase the volume produced during a given cycle include:

- Available product storage tankage
- Customer discounts for high volume
- Schedule of arriving blend stocks
- Operating shift schedules
- Cost and amount of waste materials

Long-term plans may be made for improving operations to maximize the usable product by:

- Modifying pipelines and process units to facilitate segregation (e.g., fill "families" of products in dedicated areas).
- Reducing off-specification blends through the use of modified methods and new technology (e.g., computer controls).
- Reformulating finished product to allow reworking of off-specification "premium" materials.
- Reducing toxic constituents by substituting less toxic base stocks or additives.

## 5.4.8 Solvents (See also Sections 5.3.2.2 and 5.5.6)

At major facilities where substantial volumes of solvents may be used, it is normally advantageous to separate out the halogenated hydrocarbon solvents. Trichloroethylene and perchloroethylene can be recovered from slop oils (after degreasing operations) by simple distillation solvent recovery stills. When practical, these solvents may be sent back to the manufacturers. Please note that the recycling of solvents may be a regulated activity.

At most marketing facilities, the volumes of chlorinated hydrocarbon solvents are normally too low to consider on-site reclamation facilities. With dedicated collection facilities, quantities acceptable to a reclamation contractor can be accumulated. Alternatively, incineration is the most viable option.

## 5.4.9 Sampling and Laboratory Wastes

All product samples tested in the laboratory should be collected and returned to storage. To recover sample oil effectively, it is necessary that samples be segregated (e.g., high

flash point from low) for reuse on-site in finished product. At the same time, spent reagent hazardous wastes should be segregated so they can be disposed of properly.

In addition, "quality" determinations on off-specification material should be performed in the laboratory to optimize opportunities for reuse.

## 5.5 Retail Facilities (Service Stations, Fast Lubes, C-Stores and Truck Stops)

While the volume of wastes at individual service stations, repair garages, C-stores, and truck stops may not be as great as that of wastes at other marketing sources, a given outlet's volume of waste can be significant, and the large total number of outlets makes these facilities prime candidates for benefitting from some of the following waste minimization practices:

- Practicing good housekeeping (e.g., avoiding spillage and completely draining all liquid containers).
- Segregating wastes.
- Recycling and reclaiming wastes.

Wastes associated with the retail category include the following:

- Used crankcase oil and other lubricants as well as transmission, brake, and steering fluids. (These may be recycled and reclaimed.)
- Parts-cleaning solvents. (These hazardous wastes require special handling.)
- Solid parts that are removed such as filters, batteries, and tires and other solids such as oily rags and dry absorbent materials.
- Spent antifreeze. (See 5.3.2.1.)
- Water from the bottom of product tanks.

Waste segregation is an important strategy for retail facilities. For example, hazardous waste can be minimized by preventing solvents (e.g., chlorinated hydrocarbons) from mixing with waste oils. Careful segregation helps preserve the value of recycled and reclaimed materials.

The following sections address specific areas where effective waste minimization practices can be utilized at retail facilities.

## 5.5.1 Underground Leaks and Product Spills

A major source of waste is underground leaks at retail stations. Wastes generated by such leaks include not only the product released but also the ground it contaminates and the waters (surface and subsurface) it pollutes.

The primary cause of these leaks in tanks and pipelines is corrosion. At new installations, underground leaks can generally be controlled by designing the system with noncorrosive materials and/or cathodic protection, and installing various leak detection devices. At existing locations, a combination of retrofit devices can be installed including cathodic protection, line leak detectors, and replacement of potential leak components of the system. Certain underground tank and product line upgrading and leak detection/spill prevention may be specifically required by federal and local regulations.

Elements in minimizing leaks from underground installations may include the following:

- Inventory record keeping is the key to early leak detection. Each location must establish accurate inventory record keeping.
- Wherever experience indicates corrosion, all underground facilities should be replaced with noncorrosive or cathodically protected materials.
- Where cathodic protection is utilized, controls must be established to assure continued maintenance of the system.
- A thorough investigation of any suspected tank or line leaks should be conducted. The cause of the leak should be determined and action to prevent any further loss should be taken.
- Tank leak testing should be conducted as necessary.
- Immediate action should be taken to prevent migration of the product whenever a leak occurs.

To minimize leak and spill-generated wastes, retail operators must be thoroughly knowledgeable of signs that indicate when product is being lost. Leaks can be detected promptly if adequate inventory records are maintained. Also, obvious signs of leakage and spills such as gasoline-soaked soils around dispensers, submersible pumps, and fill manholes should be investigated immediately.

Spills and leaks under the dispensers can be minimized by frequent inspections, containment manholes, avoiding spillage during filter cartridge changes, and keeping all pipe connections tight.

## 5.5.2 Underground Tank Water Bottoms

Any water that accumulates in storage tanks must be removed as often as necessary to keep its level sufficiently low so that it will not be drawn into the suction stub and to reduce water contact with alcohol components in gasoline. As a result of the contact with gasoline, the water contains gasoline additives and alcohols and it often has a chemical oxygen demand (COD) in excess of 15,000 ppm. Because of this direct contact with gasoline, the water may be hazardous under the toxicity characteristics rule and should be handled accordingly.

To prevent water from accumulating in underground tanks, the following safeguards may be considered:

- Whenever possible, check the delivery truck for water before accepting any product.
- Grade the yard area down and away from the manholes to prevent water from pooling in the area.
- Install the manhole and gauge hatches above the surrounding grade.
- Maintain and replace worn or missing gaskets or manhole covers and fill-pipe fittings.
- Ensure that caps are tightly replaced after gauging and product deliveries.

## 5.5.3 Car Wash (See also Section 5.3.2.5)

Car washes in combination with retail outlets, especially gas and go and/or C-Stores, are common and represent almost a standard facility design for much of the industry.

Detergents and chemical additives used in car washes may present treatment problems. Because these chemicals form emulsions with oil and grease washed off vehicles, they are not acceptable for discharge to the environment and may require treatment before being accepted by municipal sewer systems.

Resolving problems about where and how to discharge chemical emulsions is an important area of waste minimization. Use of a "closed system," where wash water is recycled and only "rinse water" and "make up water" are newly added completely eliminates any discharge to the environment or sanitary sewers.

Aeration and chlorination of the holding tank may be necessary to prevent an anaerobic condition from developing in the collection tank.

Accumulated sludge (i.e., sand and dirt that settle out in the holding tank) will have to be removed occasionally and disposed of by an authorized contractor in an acceptable manner.

## 5.5.4 Used Oil (See also Section 5.3.2.3)

Used oil is generated primarily at full-service stations, fast lubes, and truck stops. It is critically important that all used oil be segregated and that no other chemicals or solvent materials be added to it.

Federal, state and local regulations must be followed in disposing of used oil. Used oil can sometimes be picked up by a local reclaimer or recycler. Depending on geographic location, the availability and cost of reclamation services will vary.

## 5.5.5 Antifreeze (See also Section 5.4.2.1)

Waste or used antifreeze would normally be generated only at full-service stations, fast lubes, repair garages, and truck stops. As indicated in Section 5.3.2.1, antifreeze has a relatively high BOD and frequently contains toxic additives that could violate receiving water standards if the antifreeze is allowed to drain to a stream or storm sewer. Discharging antifreeze to an on-site sewage treatment facility could have detrimental effects on the system's efficiency and perhaps cause problems with its operation. In general, it is recommended that waste antifreeze be segregated in a separate tank and transferred to an antifreeze recycling facility, if one is available, or to an appropriate treatment facility. Please note that recycling of antifreeze may be a regulated activity.

## 5.5.6 Solvents (See also Sections 5.3.2.2 and 5.4.8)

Solvents are used primarily in parts and equipment cleaning and degreasing during maintenance and engine repair at full-service stations, repair garages, and truck stops. The limited amounts required would normally not support the cost of a package unit for recycling dirty solvents at the facility.

Spent solvents should not be added to waste oil or antifreeze. The most desirable option for their disposal is regular use of a solvent recycling company that picks up dirty solvent and leaves clean solvent for the facility. Please note that the recycling of used solvents may be a regulated activity.

## 5.5.7 Tires

Where tires are sold and/or installed, used tires become a solid waste that is somewhat difficult to dispose of and is usually unacceptable in ordinary trash. Tires should be segregated from all other trash and stored neatly to minimize space required. Service agencies are usually available for a fee to pick up tires for disposal. Care should be exercised to see that a service agency is properly and legally disposing of the waste tires.

Various industries use waste tires in many different ways, usually after some type of processing. For example, tires can be used in the construction of fill retaining walls or artificial saltwater reefs. Companies that use waste tires may provide pick-up service free of charge or perhaps even buy the waste tires.

## 5.5.8 Batteries

Used batteries are difficult to handle. They must be carefully segregated from other trash, and neatly stored in stacks, top side up, to minimize space requirements and to avoid spilling acid from inside the battery onto surrounding surfaces.

Batteries cannot be sent to landfills; rather, they must be collected by reclaimers. Collection is usually not a problem, but depending on a facility's geographic location, the frequency of pickup affects the stored volume, prices paid for used batteries and fees charged for pickup vary greatly. Much of the material in used batteries constitutes a recyclable resource. Please note that the recycling of used batteries may be a regulated activity.

# 5.5.9 Oily Solid Waste (Filters, Sumps, Rags, Empty Containers and Absorbent)

Other generally oily solid wastes, such as filter cartridges, rags, empty oil containers, solids removed from service bay sump and other oily absorbent material should be kept segregated. Oily solid wastes can be minimized by careful segregation and can then be disposed of in accordance with appropriate regulations.

Metal and/or engine parts, when kept segregated, can be sold to a metal salvage dealer. Sometimes it is also possible to sell used oil filters to metal salvage dealers. Using an oil filter compactor to crush the filters often makes this easier to accomplish. In addition, sometimes oily rags can be sent to an industrial cleaner as a means of recycling.

Any normal rubbish accumulation, such as paper, bottles, and cans may be sent with garbage to most sanitary landfills.

## Marketing Waste Minimization Practices Case Study 5-1: Asphalt Waste Recycling

### Introduction

A large West Coast asphalt producer generates about 100 barrels per year of hazardous asphalt waste. Sources of this waste are predominantly:

- Laboratory samples
- Pump seal leaks
- Valve packing leaks
- Flange leaks

Asphalt waste is typically put into sealed drums and stored on-site until transportation by a licensed hazardous waste hauler is arranged, and an appointment is made with a Class 1 dump.

## **Description of Waste Minimization Practice**

Waste asphalt is regularly collected from around the refinery and laboratory. A heating kettle is located near a source of 120 psi steam and close to the main asphalt feedline. (See figure C-5-1.)

The asphalt waste is liquefied in the kettle in 60-gallon batches. It is passed through three progressively finer mesh strainers and then routed to the main asphalt feedline.

The refinery produces both anionic and cationic asphalt. Waste asphalt is always a mixture of the two asphalts. Because cationic and anionic asphalt have different specifications, it is important to limit the amount of waste added so that product quality is not affected. Limiting waste asphalt to less than 1% of the final product precludes any noticeable product quality degradation.

### Effectiveness

Recycling of waste asphalt completely eliminates the costs associated with the transporting, manifesting, disposing, record keeping, and reporting of a hazardous waste. No detrimental effects of this practice have been reported by the refiner.

The recycling of approximately 100 barrels per year of waste asphalt produces savings of over \$220 per barrel, or over \$22,000 per year.

## Costs

Capital costs are minor (less than \$10,000). Operating costs include steam heating costs, operator man-hours, waste collection costs, and maintenance costs.



## Marketing Waste Minimization Practices Case Study 5-2: Recycling of Soap Dust Waste

## Introduction

An emulsion asphalt manufacturer uses three kinds of soaps as feedstock -- one in liquid form and the other two in a powdered form. The soap is used as an emulsifier to help suspend the asphalt in the water. Either of two soap feedstocks is typically produced, depending upon product specifications. An acidic feedstock is made by mixing the soap with water and a low-pH component. A caustic feedstock is manufactured by combining the soap, water, and a basic (high-pH) material. The resultant soap mixture is then heated and mixed using pressurized steam.

A common baghouse is used to collect the uncontrolled fugitive emissions of caustic or acidic soap particulate matter. Approximately 7 Bbls per year of hazardous soap dust waste, consisting of 98% solids and 2% water, is collected in the baghouse. This material is considered a hazardous waste because of its corrosivity, owing to either low or high pH.

## **Description of Waste Minimization Practice**

Use of a common baghouse eliminates the possibility of recycling the soap dust because the two dissimilar soap dusts are combined and other particulate matter is introduced. The waste minimization practice is based on recycling the hazardous soap dust back to the soap mixing tank.

To implement the recycling procedure, half-horsepower air blowers with bag filters are installed above each covered soap solution mixing tank. Before adding powdered soap, the blower is activated. Negative pressure draws the fugitive dust particles into the bag filters. After each soap feedstock is prepared and the mixing tank is emptied, the recovered soap dust particles are shaken from the bag filters. Segregating each soap type with its respective mixing tank allows the soap to be reused.

## Effectiveness

Elimination of a common baghouse precludes costs associated with transporting, manifesting, disposing, record keeping, and reporting of a hazardous waste. Maintaining segregation of the two powdered soap waste types allows their reuse and reduces raw materials costs.

## Costs

Costs of the soap dust recycling system include two half-horsepower blowers, two bag filters, electricity, and employee time.

## **Bibliography**

- American Petroleum Institute. May 1988. Evaluation of Treatment Technologies for Listed Petroleum Refinery Wastes. (Publication No. 4465).
- Atkins, W. and Thomas P.E. (Mittelhauser Corporation). January 1989. Management of Spent Refinery Catalysts. Western Oil and Gas Association, Laguna Hills, California.
- November, 1987. Chemical Manufacturers Association. Waste Minimization Workshop, Volumes I-II, New Orleans, Louisiana.
- Electric Power Research Institute. April 1986. Selective Catalytic Reduction for Coal-Fired Power Plants-Pilot, Final Report.
- Electric Power Research Institute. October 1984. Selective Catalytic Reduction for Coal-Fired Power Plants: Feasibility and Economics, Final Report.
- Environmental Planning and Management Committee, Canadian Petroleum Association. January 1984. Waste Disposal Guidelines for the Petroleum Industry.
- Haverhoek, S., Management of Hazardous Wastes in the Oil Refinery Industry. Shell International Petroleum Health, Safety and Environment Division, Maatschappij, The Netherlands.
- Hollod, G. J. and McCartney, R. F. (E. I. du Pont de Nemours & Co., Inc.). 1988. "Hazardous Waste Minimization: Part I, Waste Reduction in the Chemical Industry, Du Pont's Approach." APCA.
- Hunt, Gary E., North Carolina Pollution Prevention Pays Program, Department. of Natural Resources and Community Development. 1988. "Hazardous Waste Minimization: Part IV, Waste Reduction in the Metal Finishing Industry." APCA.
- Kaminski, Joseph A., "Hazardous Waste Minimization: Part VII (B), Hazardous Waste Minimization within the Department of Defense." Office of the Deputy Assistant Secretary of Defense (Environment).
- Oman, Daniel E. (RMT, Inc.). 1988. "Hazardous Waste Minimization: Part VI, Waste Minimization in the Foundry Industry." APCA.

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- Petroleum Association for Conservation of the Canadian Environment. November 1986. <u>Waste Management Guidelines for Petroleum Refineries and</u> Upgraders. (Report No. 86-2). Ottawa, Ontario.
- "Reducing RCRA Impact Through Waste Minimization." Workshop Sponsored by the American Petroleum Institute and National Petroleum Refiners Association, Arlington, Virgina, May 1987.
- Tower Conference Management Company. 1987. <u>Proceedings of The Third</u> Annual Hazardous Materials Management Conference/West.
- U.S. Department of Commerce. 1986. <u>Report to Congress: Minimization of</u> <u>Hazardous Waste</u>. Volume I and Appendices.
- U.S. Department of Commerce. 1986. <u>Waste Minimization Issues and Options</u>. Volumes I-III.
- U.S. Department of Commerce. 1987. <u>Report to Congress: Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy</u>. Volumes 1-3. (NTIS).

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## **APPENDIX A**

## **QUESTIONNAIRE AND INSTRUCTIONS**

A-1

### AMERICAN PETROLEUM INSTITUTE WASTE MINIMIZATION PRACTICES

#### INSTRUCTIONS FOR COMPLETING FACILITY QUESTIONNAIRE

The enclosed questionnaire has been developed to obtain information on successful waste minimization practices used in the oil industry. Information from the responses will be used to prepare descriptions of these practices for the Compendium of Waste Minimization Practices. Confidential or proprietary information should not be included in the response.

Upon receipt of each response, Mittelhauser Corporation will assign a facility code, which will be used to reference the response. Facilities will not be identified in the Compendium by company name or location, only by code. The actual facility identities may only be obtained by submitting a written request to API.

The objective of this questionnaire is to obtain information on successful procedures that minimize the quantity and/or toxicity of residuals/wastes from oil industry operations. Responses are requested for hazardous as well as nonhazardous residuals/wastes, including those from production and marketing, refinery catalysts, and spent chemicals that are not currently hazardous under RCRA. Some of these residuals/wastes could be considered hazardous under state regulations.

Information is requested on successful minimization practices in to the following categories:

o Source reduction
o Recycling
 - Unit
 - Facility
 - Off-site
o Treatment

Source reduction includes practices that reduce the quantity or toxicity of the waste at the source. An example of source reduction is the decreased use of sand blasting that results in solids being swept or flushed into a wastewater system. A second example would be using a street sweeper to remove dry solids that would otherwise be released into the facility wastewater system. API is particularly interested in obtaining information on successful source reduction practices.

Recycling is based on the API definition and includes

(1) the recovery of a complete residual/waste to be fed

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to a process unit or facility replacing part of its normal feedstock, and

(2) the recovery of a valuable component from a residual or waste and returning this component to a process unit or facility replacing part of its normal feedstock (reclamation).

Recycling encompasses unit, facility, and off-site recycling. Unit recycling includes a minimization practice that recovers a residual/waste or a valuable constituent from the residual/waste at the unit where it is generated and returns the recovered material as a feed to that unit. An example is recovery of a waste oil at a production site that is fed into the crude processing train.

Facility recycling may include the recovery of a waste oil from any refinery process unit and returning that oil to crude charge or injecting sludges into a coker. Another example would be returning recovered oil from an oily sludge filtration unit to crude charge.

Off-site recycling includes transporting a residual/waste to another facility to be used as a feedstock. Examples of this type of activity would be shipping a catalyst to a reclaimer for recovery of valuable metals or shipment of a spent caustic to a pulp and paper facility for use as a raw material.

Treatment includes practices that do not result in source reduction or in recovery of a useful, recyclable constituent. Examples of treatment practices are incineration and land treatment.

The questionnaire contains three separate sections and one figure. The sections request information on (1) the facility that generates the residual/waste, (2) the residual/waste of interest, and (3) the minimization practice. Figure 1 is used to help define influent, treated product, and other residual streams associated with the minimization practice.

The residual/waste section requests information on the residuals/wastes for which minimization practices are used. The residual/waste and waste minimization practices sections should be completed as a set. If more than one residual/waste is treated separately by a minimization practice, complete more than one residual/waste section and attach it to the corresponding practices section. Likewise, if more than one minimization practice is being used to treat one residual/waste or the same group of residuals/wastes, complete the appropriate number of residual/waste sections and attach them to the corresponding minimization practice sections.

The following are instructions for completing each section. Please read all of the instructions before completing the questionnaire. Two examples of completed questionnaires are

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attached to these instructions. Example "A" covers a hypothetical case where a refinery installed a pressure filter system to dewater tank bottom sludge in order to reduce the amount and cost of outside disposal. Example "B" covers a hypothetical case of oil from tank cleaning which avoided the need to scrape up and dispose of oily dirt to outside facilities.

#### FACILITY INFORMATION SECTION

The facility information section requests information on the facility using a particular waste minimization practice. These data will facilitate understanding of the quantity of residuals/wastes generated.

F1. Enter the name of the person completing the form; the company name, location, and address; and, the telephone number of the individual either completing the questionnaire or coordinating its completion if several individual are involved.

The facility code should be left blank; it will be assigned by Mittelhauser upon receipt of the completed questionnaire.

F2. Identify the capacity of your facility according to the categories shown. Please use the units given.

#### RESIDUAL/WASTE INFORMATION SECTION

This section requests information on the residual(s)/waste(s) of interest. As previously discussed, more than one residual/waste section may be completed for one minimization practices section. The appropriate residual/waste section(s) should be attached to the corresponding minimization practices section(s) as a set.

If several wastes are treated by one minimization practice and a composite analysis is available, just complete one residual/waste section. If the wastes are not treated together or a composite analysis is not available, complete separate residual/waste sections.

- R1. Identify the residual/waste stream(s) that are described on that sheet. Try to use common industry terms for describing the waste rather than names that are unique to your facility.
- R2. List the source(s) of the residual(s)/waste(s), e.g. a process unit or a particular operation or maintenance activity. If one piece of equipment is the sole source, please list the unit and equipment name.
- R3. Please list annual quantities produced prior to implementation of the waste minimization practice. Use units shown if possible.
- R4. State past management method prior to use of the

residual/waste minimization practice.

R5. Check whether the residual/waste is a solid, liquid, or sludge. If the waste is unusual, please describe it in the "other" category. For mixtures of phases, such as sludges or emulsions, please give the approximate overall composition. State the analytical method number that was used to obtain the data. Also list the extractant (like freon, methylene chloride, or THF) that was used to extract the oil phase of the sample.

Also provide available information on the concentration of metals or organic constituents that could be of interest.

#### WASTE MINIMIZATION PRACTICES SECTION

This section requests information on a particular minimization practice. As previously discussed, this section should be attached to the applicable residual/waste information section(s).

- P1. Give the name, or describe, the minimization practice of interest. Examples could be oily sludge filtration, reduction in the quantity of surfactants used for cleaning in the refinery, use of an amine reclaimer, thermal stripping of contaminated soils, etc.
- P2. Check the proper classification of the practice described. For recycling, check whether unit, facility, or off-site.
- P3. If the practice is a process, piece of equipment, or a purchased commodity that is available from a licensor or manufacturer, give that organization's name, address, and telephone number.
- P4. Some waste minimization practices of interest in this project have been used commercially; others have been tested on a pilot or demonstration scale. Please check the appropriate box.

Questions P5 through P10 request cost and performance information on your particular waste minimization application.

P5. List the capacity of the practice used. For a process unit or piece of equipment, this amount would be the capacity of the unit. For example, for catalyst recycling list the total quantity of catalyst sent to that recycler; if a dry sweeper is used to capture solids before they are released into the wastewater drains, give the quantity of solids captured per unit of time; or if a consumable raw material is replaced by another material that will result in waste minimization, list the quantity of the original material. If the practice is only laboratory-scale, please indicate such and give the extrapolated production-level amount anticipated.

P6. Check whether the practice results in a reduction in residual/waste quantity, toxicity, or both.

If the practice involves a capital expenditure, please complete question P7. If the practice involves only procurement of a service or different consumable material, please complete question P8 instead.

- P7. For a practice that requires a capital expenditure, give the capital cost of the unit or equipment corresponding to the installed capacity given in P5. Next, provide the requested information on operating requirements as appropriate. Please do not give costs for utilities. These costs can vary significantly from plant to plant. Please provide the unit cost for chemicals along with a description and supplies name. Please leave no blanks; use N.A. if not applicable or "unknown" where applicable.
- P8. This section should be completed if the practice involves only the use of a service or consumable material; e.g., if FCCU catalyst is sent to a cement manufacturing facility rather than to a disposal site. Another example is the use of sodium hydroxide to neutralize an acid stream instead of lime to avoid production of a sludge.

Describe the operation prior to application of the minimization practice. Also give unit costs per barrel, pound, etc., and annual costs for either services or consumable materials. Provide the same information after application of the minimization practice.

P9. This item requests information on a block flow diagram to determine the overall effectiveness of the practice and to assess the characteristics of any secondary wastes, emissions, or effluents that are produced. Figure 1 should be completed to understand the waste practice.

**Stream #1** is the residual/waste that is subject to the minimization practice.

Stream #2 is the minimized residual/waste. Please designate the method for its disposal or recycling. For example, filter cake from a sludge filtration unit could be designated for disposal to an off-site landfill. If this same stream is sent to a coker for injection, the designation would be "recycled to coker."

Stream #3 is used to designate a chemical that is used as part of waste minimization, e.g. be lime bodyfeed used as part of a filtration operation.

Stream #4 is used to designate any air emissions directly related to the practice.

A secondary stream, such as a wastewater stream that is separated from the residual/waste as a consequence of the minimization practice, is designated as Stream #5. Please

designate whether it is treated, recycled, or disposed, and briefly describe the method.

- P10.If information is available on the environmental characteristics of any product or residual stream described in P9, please provide data. Use a separate copy of the P10 page for each stream from P9 for which data are available.
- P11.Please provide any additional descriptive information that will assist in understanding the minimization practice.



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## WASTE MINIMIZATION PRACTICES QUESTIONNAIRE

## FACILITY INFORMATION SECTION

F1. PERSON COMPLETING FORM	FACILITY CODE _	
COMPANY NAME		
LOCATION		· · · · · · · · · · · · · · · · · · ·
ADDRESS		
TELEPHONE	•	
F2. FACILITY SIZE:		
MARKETING FACILITY: Storage Capacity,	bbls	
REFINERY: Crude Charge, bpsd		
PRODUCTION FACILITY: Crude and Condensates Produced,		bpd

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### WASTE MINIMIZATION PRACTICES QUESTIONNAIRE

## RESIDUAL/WASTE INFORMATION SECTION

R2. R3. R4.	SOURCE (UNITS ANNUAL QUAN MANAGEMENT	S) TITY PRODU METHOD WI	CED		tpy	r, bbl/yr (Circle One
R5.	RESIDUAL/WAS	TE CHARAC	TERIZATION:			<u> </u>
	WASTE TYPE: (0	Check One)	Solid	Liquid	Slud	ge
	COMPOSITION:	% OIL % SOLIDS % H₂O		METHOD METHOD METHOD METHOD	EXT	RACTANT
	Antimony — Arsenic — Barium — Beryllium — Cadmium — Chromium (+6) — PRIMARY HAZAF		Chromium (+3) Cobalt Copper Fluoride salts Lead Mercury Molybdenum		Nickel Selenium Silver Thallium Vanadium Zinc Asbestos	
	Cc	onstituent		Estim. TOTAL	ated Concentr	ations, ppm TCLP

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## WASTE MINIMIZATION PRACTICES QUESTIONNAIRE

### WASTE MINIMIZATION PRACTICES SECTION

#### P1. MINIMIZATION PRACTICE

-

	ATTACH A DESCRIPTION OF MINIMIZATIO	N PRACTICE AND GENERAL FLOW SKETCH, IF
P2.	CLASSIFICATION (CHECK):	
	SOURCE REDUCTION	
	RECYCLING UNIT FACILITY OFF-SITE	
	TREATMENT	
P3.	VENDOR FOR WASTE MINIMIZATION PRA	CTICE
	VENDOR	NAME
	ADDRESS	
	TELEPHONE	
P4.	TYPE OF USE (CHECK ONE):	
	COMMERCIAL TEST	
P5.	CAPACITY:	
P6.	TYPE OF REDUCTION ACHIEVED:	QUANTITY TOXICITY BOTH OF ABOVE
P7.	PROCESS UNIT OR EQUIPMENT COSTS:	
	ESTIMATED CAPITAL COST.	
	OPERATING REQUIREMENTS:	
WAT		gallons per day
ELE	CTRICAL	gailons/barrel of waste feed kwh or Hp kwh or Ho/barrel of waste feed
STE	AM	pounds per hour @ PSIG
AUX		pounds/barrel of waste feed gpm, COST\$/gal gpm, COST\$/gal gpm, COST\$/gal

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FUEL OPEF MAIN	RATING LABOR	BTU/HR BTU/barre men/shift % of capita	of waste feed
C -	comments regarding process operations:		
- - - P8. S	SERVICES OR CONSUMABLE MATERIAL	S:	
- 	OPERATION PRIOR TO MINIMIZATION		
C 	OPERATION AFTER WASTE MINIMIZATIO	N	
L A	JNIT COST OF SERVICE: ANNUAL COST OF SERVICE:	Prior to Waste Minimization V	After Vaste Minimization
L A	JNIT COST OF CONSUMABLE MATERIAL	:	

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### WASTE MINIMIZATION PRACTICES QUESTIONNAIRE

WASTE MINIMIZATION PRACTICES (CONT)

STREAM NU:				
WASTE TYPE: (0	Check One)	Solid	_ Liquid	Sludge
		Other	, describe	
COMPOSITION:	% OIL			EXTRACTANT
	% SOLIDS	·····	METHOD	·
	% H₂O		METHOD	
METAL CONCEN	ITRATIONS	(indicate ppm under	r applicable toxicity	r test)
	EP   TCLP		EP TCLP	EP   TC
Antimony		Chromium (+3)		Nickel
Arsenic		Cobalt		Selenium
		Copper		Silver
Barium		Fluoride salts		
Beryillum Codmium -				
Caumum		- Molubdonum		
			والمحالي المتحدث المحالي فتتلك محدد المحال المتحد المحالي المحالي المحالي المحالي المحالي المحالي المحالي المح	
PRIMARY HAZAR		- ANIC CONSTITUEN		l.
PRIMARY HAZAF	RDOUS ORG	 ANIC CONSTITUEN	TS OF CONCERN	l:
PRIMARY HAZAF	RDOUS ORG	 ANIC CONSTITUEN	TS OF CONCERN Estin	l: nated Concentrations, ppm
PRIMARY HAZAF	RDOUS ORG	 ANIC CONSTITUEN	TS OF CONCERN Estin TOTAL	l: nated Concentrations, ppn TCLP
PRIMARY HAZAF	RDOUS ORG	ANIC CONSTITUEN	TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG	 ANIC CONSTITUEN	TS OF CONCERN Estin TOTAL	I: nated Concentrations, pp <del>n</del> TCLP
PRIMARY HAZAF	RDOUS ORG	ANIC CONSTITUEN	TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG	ANIC CONSTITUEN	TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG	ANIC CONSTITUEN	TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppm TCLP
PRIMARY HAZAF	RDOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppm TCLP
PRIMARY HAZAF	ADOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG	ANIC CONSTITUEN	TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	RDOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	ADOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP
PRIMARY HAZAF	ADOUS ORG		TS OF CONCERN Estin TOTAL	I: nated Concentrations, ppr TCLP

# P11. PLEASE PROVIDE AVAILABLE INFORMATION LIKE DESCRIPTIONS, FLOW DIAGRAMS, CASE STUDIES, ETC., TO AID IN UNDERSTANDING THE MINIMIZATION PRACTICE.

## **APPENDIX B**

## LETTER OF TRANSMITTAL FOR PRODUCTION, REFINING, AND MARKETING

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(TRANSMITTAL LETTER FOR EXPLORATION AND PRODUCTION)

Date

Name Street State

Salutation:

The American Petroleum Institute (API) has retained Mittelhauser Corporation to prepare a study of waste minimization practices at petroleum industry facilities. This survey is part of API's program to encourage waste minimization in the petroleum industry. API believes that, given the costs and future liabilities associated with disposal, waste minimization will play a critical role in managing our industry's wastes. Furthermore, both EPA and Congress have stated that industry should aggressively minimize its wastes.

This study will document waste minimization practices that have been successfully used at petroleum facilities to reduce the quantity or toxicity of residuals/wastes that are generated. The goal of this project is to describe the range of industry practices rather than to select or prescribe any one standard practice or practices.

As part of this contract, API has requested that Mittelhauser conduct a survey of selected petroleum industry facilities to obtain information on successful waste minimization practices. In this regard, we request that you complete the enclosed survey questionnaire and return it to Mittelhauser

Corporation at the following address:

Mittelhauser Corporation Attn: Herb Morgan 23272 Mill Creek Road, Suite 300 Laguna Hills, CA 92653

Upon receipt of each response, Mittelhauser Corporation will assign a facility code, which will be used to reference the response. Facilities will not be identified in the compendium by company name or location, only by code. The actual facility identities may only be obtained by submitting a written request to API. API PUBL\*302 91 🎟 0732290 0529129 481 📟

We are particularly interested in minimization practices related to the following wastes:

- Solvents and chemicals
- Tank bottoms and other oily sludges
- Scrubber solutions
- Work-over fluids
- Diatomaceous earth
- Completion fluids
- Stretford solution
- Filter media and cartridges
- Maintenance debris
- Weed killers
- Used lube oil
- Spent acids or caustics
- Spent catalysts
- Spent amines and glycols
- Oily dirt and
- Iron sponge
- Molecular sieves

As discussed in the instructions, your responses should include minimization practices that are used on nonhazardous as well as hazardous wastes. Also, please consider and submit responses on all practices you may use, even if they are not listed above.

If you have any questions regarding completion of this questionnaire, please call either Mr. Tom Atkins or Mr. Herb Morgan of Mittelhauser at (714) 472-2444. If you have questions regarding the reasoning or conceptual background for this program, please call me at (202) 682-8477. We request that your questionnaire be completed and mailed to Mittelhauser by May 11, 1988.

Sincerely,

Paul S. Price Senior Regulatory Analyst

PSP: P979AI

B-3

(TRANSMITTAL LETTER FOR REFINING)

Date

Name Street State

Salutation:

The American Petroleum Institute (API) has retained Mittelhauser Corporation to prepare a study of waste minimization practices at petroleum industry facilities. This survey is part of API's program to encourage waste minimization in the petroleum industry. API believes that, given the costs and future liabilities associated with disposal, waste minimization will play a critical role in managing our industry's wastes. Furthermore, both EPA and Congress have stated that industry should aggressively minimize its wastes.

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We are particularly interested in minimization practices related to the following wastes:

- Oily sludges
- Stretford solution
- Amine sludges
- Acid sludges
- Chemical sludges
- Solvents and chemicals
- Spent catalysts
- Spent caustic
- Filter clays and cartridges
- Tank bottoms
- Alky sludge
- Biosolids
- Off-test lubes and greases
- bundle cleaning sludge
- heater decoking and
- maintenance debris

As discussed in the instructions, your responses should include minimization practices that are used on nonhazardous as well as hazardous wastes. Also, please consider and responses on all practices you may use, even if they are not listed above.

If you have any questions regarding completion of this questionnaire, please call either Mr. Tom Atkins or Mr. Herb Morgan at (714) 472-2444. If you have any questions regarding the reasoning or conceptual background for this program, please call me at (202) 682-8477. We request that your questionnaire be completed and mailed to Mittelhauser by May 11, 1988.

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PSP: P979AJ

(TRANSMITTAL LETTER FOR MARKETING)

Date

Name Street State

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> Mittelhauser Corporation Attn: Herb Morgan 23272 Mill Creek Road, Suite 300 Laguna Hills, CA 92653

We are particularly interested in minimization practices related to the following wastes:

- Contaminated fuels and lubricants
- Contaminated soils
- Tank bottoms

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- SPCC tank bottoms
- Truck washing
- Truck "retains"
- Maintenance activities and
- Spent filter cartridges

As discussed in the instructions, your responses should include minimization practices that are used on nonhazardous as well as hazardous wastes. Also, please consider and submit responses on all practices you may use, even if they are not listed above.

If you have any questions regarding completion of this questionnaire, please call either Mr. Tom Atkins or Mr. Herbert N. Morgan at Mittelhauser Corporation at (714) 472-2444. If you have any questions regarding the reasoning or conceptual background for this program, please call me at (202) 682-8477. We request that your questionnaire be completed and mailed to Mittelhauser by May 11, 1988.

Sincerely,

Paul S. Price Senior Regulatory Analyst

PSP: P979AK

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Order No. 849-30200



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