Petroleum refinery waste management and minimization

An IPIECA Good Practice Guide
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Executive summary

Optimized, effective waste management is integral to petroleum refinery operations. It helps minimize risk to both people and the environment, enhances resource utilization, and can also reduce costs. This document provides a comprehensive and practical guide to refinery waste management, detailing waste types, waste characterization, and key management processes and technologies.

Many countries have detailed legislative requirements and control systems that apply to all aspects of waste management, while others have less regulatory oversight and guidance. Designed primarily to aid refinery waste management in countries with less (or no) regulatory oversight and guidance, this guide will also be of use to any refinery targeting enhanced waste management performance.

A section on sources of waste describes four broad categories of solid waste generated by refineries—process waste, maintenance and operational wastes, commercial waste and medical waste where appropriate—and details the types of waste in each category. The guide outlines the processes for identification and quantification of solid waste streams, and underlines the importance of understanding waste generation cycles in planning and implementing appropriate waste management. Refinery wastewater treatment and the wastes produced from it are covered in detail in the related IPIECA document, *Petroleum refining water/wastewater use and management*.

The guide discusses the importance of characterization of refinery waste streams, to enable regulatory classification, as well as the identification of potential health, safety or environmental risks related to waste storage, transport, processing and disposal. It explores waste sampling and analysis, and includes links to US EPA and European Union websites related to waste characterization.

A section explores how and why waste minimization should be incorporated into all
refinery waste management systems to identify opportunities to prevent or reduce waste generation. The guide also looks at waste treatment options that can reduce any potential impacts at the disposal stage. Activities that can help to reduce wastes and attendant hazards are differentiated and their terminology defined.

Waste streams that cannot be reduced, reused or recycled will typically be managed on-site or off-site through a combination of storage, treatment and disposal methods. The guide describes the options and stages for storage, treatment and disposal, and underlines the importance of full documentation in enabling compliance with any applicable legislation, and in minimizing the risks of exposure of personnel to hazardous substances and the potential for contamination of soil and groundwater.

A discussion of on-site and off-site treatment and disposal issues is included. Recognizing that waste management does not stop at the refinery gates, and often involves third-party contractors for transport, treatment and disposal, the guidance emphasizes the importance of using support services with appropriate qualifications, expertise, equipment and sites, and maintaining full chain-of-custody documentation.

To ensure continuous, effective waste management, refineries should consider operational audits of on- and off-site waste management facilities and activities, including the equipment, sites and activities of waste contractors. The guide’s final section outlines the auditing process and key considerations, while emphasizing the importance of regular operational audits, and/or auditing before and after contracts are agreed, and/or when they are amended or renewed.

The guide includes flowcharts of key processes, checklists of key considerations and explanations of key terms, which can help to identify both improvement priorities and management options for typical refinery waste streams. An extensive annex details refinery processes and associated descriptions.
Effective waste management is an integral part of the operation of a petroleum refinery. Optimizing the management of waste helps to minimize risk to people and to the environment, makes more effective use of resources and, in some cases, can reduce costs.

In many countries, detailed legislative requirements apply to all aspects of waste management, with each country employing its own unique system of controls. However, in other countries, far less regulatory oversight and guidance exists. This guidance is intended primarily for refinery waste management in countries with less (or no) regulatory oversight and guidance, and to assist local management to improve their waste management performance, if needed.

This document describes a variety of design, operational, equipment and procedural elements that can be considered to help define a waste management system, identify priorities for improvement and highlight waste management options for waste streams typically produced at a refinery.

The design and operational elements and equipment referred to are provided as options for consideration and should not be interpreted to be applicable as standard operation in all refineries. When considering the applicability of any particular technique, site-specific factors including as-built facility design limitations, government regulatory requirements and lack of commercially available waste management infrastructure should be taken into account.

The term ‘waste’ is used in this document to generally define any liquid or solid residue from site refinery operations, other than a petroleum product, for which there is no economically viable outlet and which therefore needs to be managed via recycling, treatment or disposal.
Optimal waste management at a refinery is best achieved by the implementation of a waste management system, either as a stand-alone combination of equipment and procedures that are applied to manage the waste materials produced, or as a part of an overall environmental management system or an integrated environment, health and safety (EHS) management system.

In order to maximize benefits to the site as a whole, integration of waste management within an overall EHS management system is preferred because the management of other environmental aspects, such as emissions to air and water, can be interrelated. It is therefore useful to periodically evaluate waste management holistically within the context of the rest of the EHS management system.

The waste management system itself should include the elements shown in Figure 1, along with appropriate training and documentation to describe the processes used and to record the outcomes. These elements are examined in more detail within the relevant sections of this document.

Key to successful implementation of a management system is site management ownership that is demonstrated by approval, commitment and leadership.

As a minimum, the facility should ensure that it complies with all local laws and regulations concerning waste management. A survey of the national laws, local regulations and any other agreements applicable to waste management and disposal practices should be completed, as

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### Figure 1 Key elements in the waste management system

- Ensure Management approval & commitment.
- Identify applicable waste regulatory requirements.
- Compile an inventory of all wastes produced.
- Characterise waste composition & identify any hazardous properties.
- Ensure the waste is stored safely.
- Evaluate waste minimisation options.
- Identify available waste management options & facilities.
- Evaluate suitability of third party waste management facilities.
- Select & implement waste management option.
- Ensure waste is transported safely.
- Establish and monitor system performance indicators.
- Review system elements periodically to identify & capture new opportunities.
these requirements will frame the specifics of the management system being developed. The relevant regulatory requirements can be compiled in a Waste Legal Compliance Register or integrated within the overall EHS management system, if the facility has developed one. Regular reviews should be carried out to ensure that any relevant changes in legislation are captured, that any necessary permits or licences are kept up to date and that facility operations remain in compliance.

Once the waste management practices required to ensure compliance with the law have been identified, the facility can then also define additional standards, procedures, equipment and external providers to develop a waste management system that fully meets all company objectives and external stakeholder requirements.

The refinery’s waste management system should ensure that personnel who handle waste and/or carry out waste management activities are trained to perform their tasks in a safe and environmentally responsible way. Key tasks and procedures for managing waste safely and minimizing impacts on the environment should be documented and maintained to ensure that they remain up to date. In some jurisdictions, personnel performing specific tasks may be required to obtain specific qualifications demonstrating competency in waste management. Personnel should be trained prior to their potential exposure to waste management activities, and should receive periodic follow-up training, to ensure continuous improvement of waste management and to prevent damage to health and environmental quality. Permanent records of training in waste management activities should be retained for auditing purposes.

Performance indicators appropriate to the design of the system implemented at the facility should be developed and stewarded to verify that the system is functioning as intended and to highlight opportunities for further improvement.
Sources of waste

Petroleum refineries generate four broad categories of solid waste: process waste; maintenance and operational wastes; commercial waste, including food wastes; and, if a medical facility is on-site, medical waste. Refineries produce industrial process wastes that are inherent to the activities they carry out in the handling and processing of crude petroleum and petroleum products. In addition, commercial wastes produced are typical of those produced by an office or warehouse, and usually consist of low-density non-hazardous waste materials, primarily packaging materials and waste office supplies. On-site food service operations may produce a food waste stream, while on-site clinics may produce small amounts of medical waste. These broad categories can be broken down more discretely as shown in Table 1.

Virtually every refinery has a wastewater treatment plant to process hydrocarbon-containing wastewater through one or more steps of primary and secondary treatment. Refinery wastewater treatment and the wastes produced from it are covered in detail in the related IPIECA document, *Petroleum refining water/wastewater use and management*.

The quantity of each waste stream should be determined either directly in mass terms (e.g. kilograms) or as a volume with the specific gravity or density of the material identified to allow for conversion to mass flow. The period of generation should also be recorded so that planning of recycling, disposal or treatment can take into account the continuous or intermittent nature of the generation of the waste as well as the overall quantity requiring management.

### Table 1 Typical petroleum refinery waste

<table>
<thead>
<tr>
<th>Waste type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process</strong></td>
<td>• Oil handling wastes—oily and non-oily sludge from tanks and process equipment (often characterized as hazardous) and sludge from wastewater treatments</td>
</tr>
<tr>
<td></td>
<td>• Oil processing wastes—spent catalysts, off-specification material, spent chemicals, unsaleable by-products, and waste treatment by-products (often hazardous)</td>
</tr>
<tr>
<td><strong>Maintenance and operational waste</strong></td>
<td>• Construction/demolition waste</td>
</tr>
<tr>
<td></td>
<td>• Residues from exchanger and equipment cleaning</td>
</tr>
<tr>
<td></td>
<td>• Expired product samples</td>
</tr>
<tr>
<td></td>
<td>• Spent solvents/paint and associated clothing, rags</td>
</tr>
<tr>
<td></td>
<td>• Spill clean-up materials and contaminated soils</td>
</tr>
<tr>
<td></td>
<td>• Used batteries, mercury lamps etc.</td>
</tr>
<tr>
<td><strong>Commercial</strong></td>
<td>• Packaging materials—uncontaminated</td>
</tr>
<tr>
<td></td>
<td>• Packaging materials—contaminated</td>
</tr>
<tr>
<td></td>
<td>• Office waste (e.g. waste paper, waste office supplies, etc.)—non-hazardous</td>
</tr>
<tr>
<td></td>
<td>• Small quantities of hazardous materials (e.g. batteries, mercury lamps, fluorescent bulbs, asbestos-containing materials, etc.)</td>
</tr>
<tr>
<td></td>
<td>• Food scraps</td>
</tr>
<tr>
<td></td>
<td>• Grease from cooking</td>
</tr>
<tr>
<td><strong>Medical</strong></td>
<td>• Small amounts of medical waste (if refinery has on-site clinic)</td>
</tr>
</tbody>
</table>
Process waste

Refineries vary in size and complexity, are generally geared to processing a particular slate of crude and, to a certain degree, also reflect the demand for specific products in their local market. The typical unit operations in a refinery are designed to convert crude oil, using physical and chemical conversion processes, into a combination of fuel products, lubricating base oils and bitumen for marketing and other intermediate products that are supplied to other facilities.

A detailed discussion of the specific processes that exist within typical petroleum refineries is provided in the Annex on page 25, with a focus on the waste streams that are significant for each process. Regardless of the fact that several of the waste streams end up being managed together, it is first important to understand each discreetly so that waste minimization opportunities are fully identified. Most of the unit operations discussed in the Annex pertain to typical refineries, but not all are present in every refinery or configured as shown in Figure 2.
The actual substances present in refinery wastes will depend upon the combination of the individual process technology used and the specific crude oils being processed. Table 2 provides general guidance for the types of substances that may be present in refinery wastes.

**Maintenance and operational waste**

Petroleum refineries periodically produce quantities of wastes that are significant due to their volume, hazardous characteristics not related to hydrocarbon processing, or because they are of a nature that makes them incompatible with direct disposal to municipal landfill. A wide variety of wastes may be generated during routine maintenance, turnarounds and other activities related to ongoing operations. These include:

- **Construction/demolition waste**: external service providers can recycle a large amount of this material, if it can be confirmed that there are no specific hazardous materials present. Uncontaminated scrap metal is particularly valuable, and broken concrete pieces can be recycled as semi-valuable waste that can be used in road building and as aggregate in the production of new concrete. Abrasive blasting residue can also be used as a replacement for aggregate in cement and concrete.

- **Asbestos-containing materials**: these require special handling and packaging to ensure that there is no escape of fibres before being deposited in a secure landfill. The disposal of asbestos should be handled with care, and should be properly separated so that it is not mixed with other hazardous or non-hazardous waste. Local requirements should be investigated, and planning for the disposal of this type of waste, including the use of an appropriate service provider for removal of the material, is essential prior to the generation of the waste.

- **Expired product samples**: these can often be recycled to the refinery slop oil system, with the containers recycled through cleaning, or crushed and disposed of with other oil contaminated debris, such as rags and personal protective equipment (PPE).

- **Spent solvents/paint**: these wastes are best minimized by simply using the solvents and paints until the containers are empty of all liquid material—as long as legitimate uses for the materials exist. Spent solvents can often be

<table>
<thead>
<tr>
<th>Category</th>
<th>Specifics</th>
</tr>
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<tbody>
<tr>
<td>Oil impacted wastes, e.g.</td>
<td>• Volatile and/or semi-volatile organic compounds potentially including benzene, toluene, ethyl benzene, xylene (BTEX)</td>
</tr>
<tr>
<td></td>
<td>• Liquid hydrocarbons/tars</td>
</tr>
<tr>
<td></td>
<td>• Heavy metals dependent upon composition of crude oil being processed, but may include nickel, vanadium, lead, arsenic, chromium</td>
</tr>
<tr>
<td>Waste catalysts</td>
<td>• Metals associated with the catalyst itself dependent upon specific catalyst and service, but may include nickel, cobalt, and molybdenum; heavy metals dependent upon composition of crude oil being processed as described above</td>
</tr>
<tr>
<td></td>
<td>• Metal sulphides</td>
</tr>
<tr>
<td>Waste gas treating solutions</td>
<td>• Dependent upon the treating process used, but may include sodium hydroxide, hydrogen sulphide, phenol, amines</td>
</tr>
</tbody>
</table>
recycled/reclaimed/re-distilled, often by third-party service providers, into fresh solvents for reuse. Where liquid paint or solvent requires disposal, it is often blended into waste fuels and burned for energy recovery, or incinerated.

- **Spill clean-up materials and contaminated soils or other media:** this includes contaminated rags, clothing and contaminated adsorbents that do not contain a free hydrocarbon phase. Contaminated materials that contain a free hydrocarbon phase should be drained and/or otherwise pre-treated to recover the free hydrocarbons prior to disposal. These wastes are typically packed in a manner that minimizes volume, and are disposed of off-site through incineration or to landfill, either as hazardous or non-hazardous waste depending on the nature of the spilled material or contamination.

**Medical waste**

Small amounts of medical waste will be produced at refineries that have an on-site medical clinic. Where medical waste is produced that would be classified as hazardous, or which may have a special designation according to local regulations, management of the material should comply with those requirements. These wastes should be stored in specific locations for this purpose, with identification and access control. The waste storage facility (or container) should allow the adequate containment of waste, cleaning and disinfection. Disposing of medical waste in cooperation with a local hospital or other appropriate medical waste facility can be a successful approach.

**Commercial waste**

For commercial waste, food waste from kitchens and non-hazardous industrial waste, waste minimization options can often be easily identified, leading to waste reduction, increased recycling and cost savings. Key to realizing these benefits will be the availability of external providers of recycling services for the recoverable materials, and the performance of the collection/segregation system.

Commercial waste such as used batteries, mercury lamps and fluorescent bulbs can often be returned to manufacturers or suppliers for recycling, or sent to commercially available recycling facilities that are able to recover the mercury or other valuable metal components. In countries where this is not possible, these can be pre-treated for volume reduction and encapsulation of hazardous materials before disposal to landfill. It is important to follow applicable disposal regulations.
Waste characterization

Every waste stream generated by the refinery should be characterized sufficiently to allow for proper regulatory classification, and the identification of any physical characteristics and/or chemical constituents that could generate a safety or environmental risk while in storage or during transport or processing of the waste, as well as any environmental or health effects resulting from its disposal. In most cases the duty of care for safe disposal does not usually end at the refinery gate: responsibility for safe disposal continues through to the point of final disposal, and off-site facilities should be evaluated to ensure that they are operated in an environmentally responsible manner, and in compliance with their national/local regulations and international norms where local regulations do not exist.

Classification of wastes may need to be performed in accordance with regulatory requirements that sometimes list specific waste streams of concern and prescribe treatment or disposal methods that are acceptable for the wastes. More often, however, wastes are classified by properties such as physical state (solid, liquid or gas) and hazardous characteristics (flammable, ignitable, toxic, corrosive, etc.) to determine how they should be handled and disposed of. Characterization requirements should therefore be identified for each waste stream on a case-by-case basis.

Where sampling is necessary to determine the properties of the waste, procedures should be implemented and documented to ensure that any handling of the waste is first assessed for potential hazards that may be reasonably foreseen, and the sampling activity managed to prevent risk of injury or exposure to hazards.

Samples should be taken to ensure that they are fully representative of the waste. Wastes may not be homogenous, for example separation into layers may have occurred, so samples should be taken from different depths within the waste wherever possible. In cases where the different parts of the waste represented by these samples cannot physically be separated for disposal, the samples can be combined to provide a composite sample for testing.

Physical properties of wastes should be determined, where appropriate, to allow for the planning of appropriate transport and treatment. The characteristics of the waste material, such as the physical state (solid/liquid), particle size and percentage of water or oil content, are often important to determine the most efficient means to handle a waste stream.

Appropriate analytical characterization of waste materials may be necessary to identify and/or confirm whether the waste exhibits hazardous properties, as well as for determining suitable management options, such as recycling/reuse opportunities, or the level of treatment that may be required. Chemical analyses for hazardous volatiles that may be released in processing are often performed. Analyses for leachable metals and toxic organics are typically performed on wastes being sent to landfill, to determine the type of landfill that is able to accept the waste.

In some cases, conducting a more detailed characterization can reduce overall waste disposal costs, for example by confirming the absence of any hazardous properties and therefore enabling less expensive disposal options to be considered.

Characterization should be done using accepted industry methods that are documented at the facility so that they can be communicated accurately and transparently to those that require the information. Again, the parameters measured and the analytical methods used will, to some extent, depend on the categories of waste segregation and the final disposal route in each case. They may also depend on the pre-treatment options available in the refinery, e.g. the availability of sludge dewatering equipment.
Typically, analysis will include, but is not limited to:

- physical characteristics (e.g. density, specific gravity, % solids, pH, flash point, loss on ignition);
- heavy metals (including organic lead if lead alkyls are, or were, used on-site);
- asbestos (e.g. from insulation);
- halogenated waste (e.g. polychlorinated biphenyls (PCBs) from transformer oil);
- pyrophoric materials (e.g. iron sulphides from heat exchanger bundle descaling);
- total organic carbon (TOC); and
- oil and grease content.

In addition to assisting in the classification of waste streams the results of this analysis will also determine whether the waste stream is necessarily classified as ‘hazardous’ in accordance with local regulations.

In the absence of local regulations specifying parameters for analysis and characterizing wastes, the links below may provide a guide to classification parameters of hazardous wastes, as applicable in the USA and the European Union:

United States Environmental Protection Agency: www.epa.gov/osw/hazard/wastetypes/characteristic.htm

The process of waste minimization should be incorporated into the waste management system of every facility, to identify ways that waste can be prevented from being generated in the first place and to reduce the amount of waste that is generated where practicable. Waste may need to be treated to reduce its potential impact upon disposal, by reducing its intrinsic hazards (e.g. toxicity, corrosiveness, flammability, etc.). Activities that can lead to the reduction of wastes and their hazards are generally differentiated, and are defined by the terminology listed in Table 3.

To determine which method of waste management is the most technically feasible and economically beneficial in comparison to other methods, an iterative process of information gathering, analysis, implementation and measurement of results should be completed with respect to every waste stream that is produced, as shown in Figure 3.

For all facilities, the first step in the minimization process is to identify significant waste streams with respect to volumes and cost, and also to identify those that present significant risk to people, assets and the environment.

Streams identified should be quantified and characterized as much as possible based on existing data and information.

After a basic understanding of the waste streams has been developed (Figure 4), the available management options should be identified with input from a team of people drawn from facility operations, maintenance, the EHS function and any available waste management contractors, as appropriate. These options can then be evaluated on the basis of expected benefits in the reduction of risk to people and the environment in comparison to their cost and technical feasibility at the location, taking into account experiences with the options at other locations.

Options worth pursuing from the cost/benefit analysis can then be implemented through changes in process or procedures, installation of equipment where required, or engagement of external service providers. Part of any

### Table 3  Waste minimization terms

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
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<tbody>
<tr>
<td>Reduce</td>
<td>A reduction in the quantity or toxicity of a waste stream at its source</td>
</tr>
<tr>
<td>Reuse</td>
<td>To make secondary use of a waste in a manner that replaces another raw material and eliminates a quantity of waste</td>
</tr>
<tr>
<td>Recycle</td>
<td>To process a waste stream into a new raw material or recover the original raw material, typically with some loss as another waste</td>
</tr>
<tr>
<td>Treatment</td>
<td>Processing of a waste stream to reduce its volume and/or toxicity, often producing a distinct waste stream of its own</td>
</tr>
<tr>
<td>Disposal</td>
<td>Final placement of a waste material in a location that is meant to be its permanent repository</td>
</tr>
</tbody>
</table>

### Figure 3  Waste minimization process

- **Information gathering**
  - Identify wastes
  - Identify volumes
  - Brainstorm options
- **Analysis**
  - Options available
  - Cost/benefit
  - Compliance issues
- **Results measurement**
  - Determine actual costs
  - Identify benefits
  - Identify problems
- **Implementation**
  - Make process change
  - Install equipment
Implementation intended to minimize a waste stream should be an improvement of the means to quantify the waste stream. This will allow the actual reduction achieved to be quantified, as changes to waste management practices are often made on the basis of assumptions or rough estimates of a waste, since there may not have been any previous incentive to establish an accurate means of waste measurement. Effectively, if it is not measured, it can't be minimized.

Finally, after the change in waste management has been in operation for a period of time, data should be collected to verify the volume and characteristics of the waste following the change, and to confirm that the benefits identified prior to the change have been achieved, along with identification of any unexpected negative aspects of the change. This information becomes the basis for the next iteration of evaluation of the waste within the minimization cycle. All waste streams should be periodically evaluated for continual improvement of the management practices as technology advances, and as the availability of external services providers and other factors (such as legal requirements) change over time.

A key concept that should be embraced when adopting a waste minimization strategy is internalization. Internalization involves approaching all wastes as assets that should be managed like any other product or raw material, particularly considering economics. This can be achieved by applying an economic value to waste minimization through key performance indicators (KPIs), setting audit procedures, accounting practices and other business processes. Wastes may be assigned a negative value in terms of their cost for accounting purposes, so that reducing them is recognized as a goal along with other targets that are expressed in monetary values.

It is also important to communicate throughout the organization the achievements of company personnel in minimizing waste and any associated benefits gained, e.g. reduced
environmental impact or cost savings. Many waste minimization programmes are ultimately proven successful or not at the point where waste generators are required to begin the waste segregation process, record initial values of a waste material, and control housekeeping practices. Therefore, gaining the motivation of these personnel is a key objective in a waste minimization strategy.

The training shall ensure that all personnel involved understand and are able to perform their waste management, control or operating duties in accordance with established company policies, procedures and applicable laws/regulations. The goal of an ongoing training programme should be to develop awareness and continuous improvement among all employees, to enable them to recognize and understand the impact of their performance on waste management programmes as well to prevent damage to health and environmental quality.

Where facilities produce recyclable streams, the contract conditions for transport and subsequent use of those streams should be evaluated to make sure that the facility gains any appropriate economic benefit wherever possible. Also, a facility that is successful in getting personnel to carry out waste segregation should ensure that its contracts for transport/waste management ensure that service providers collect segregated recyclable material separately from other wastes to maintain and enhance employee motivation.

**General practices and housekeeping**

A good holistic approach to waste management includes examining general practices to prevent waste production throughout the facility. Attention to good housekeeping is important for many of the functions within a refinery (process operation, maintenance, administration, etc).

Regular clean-up of work areas enables the identification of small spills and waste that has not been properly disposed of.

Other general practices that apply to all types of waste generation and management include:

- draining raw material vessels and process equipment fully;
- regular maintenance of equipment to prevent waste generation;
- minimizing the use of cleaning chemicals, taking care when weighing and transferring chemicals to minimize spills, and selecting the least hazardous chemicals that are suited to the application;
- use of dry sweep approaches rather than water wash (minimizes wastewater management);
- minimizing the amount of solids entering refinery process sewers, to reduce waste generation and maintenance costs associated with cleaning, removal and disposal of solids/sludge from the wastewater treatment system; street sweeping to minimize the amount of solids allowed to enter the sewer is one key activity;
- organization of storage and logistics activities to prevent waste generation; and
- planning of major maintenance to minimize disturbance at the refinery wastewater treatment plant, and making appropriate use of the treatment provided by the wastewater treatment plant for aqueous wastes.

**Waste documentation**

A system is required to document waste generation and to communicate chain-of-custody transfers between parties involved in the waste management process. A documentation system also identifies the final disposition of wastes for communication to government regulators, and provides a due diligence demonstration in legal jurisdictions where strict liability is applied to waste...
A documentation system is an essential element for all facilities and should be made mandatory in contracts with third-party waste management service providers.

Documentation can be in either hard copy or electronic format. The documentation system should keep a step-by-step record of the process of waste disposal, and should also record the quantity of the waste as chain-of-custody transfer occurs. An example of a ‘five-docket’ documentation system is shown in the Figure 5.

In the ‘five-docket’ records system shown in the figure, a five-part multicoloured form is filled out, in order, by the waste generation, transportation, treatment, recycle and disposal parties involved in the operation. A unique record is generated for each waste stream being managed at a facility. Although the record can be used by the generator to document the amounts of waste recycled, treated and disposed of on-site at its facility, the form is primarily designed to record the characteristics and quantities of waste that are transferred off-site for recycling, treatment or disposal.

The documentation process illustrated in Figure 5 takes place as follows:

- The generator of the waste completes the first section of the form and removes the top copy (1). The remainder of the form is then forwarded, together with the waste (and with any other manifesting requirements) to the transportation company.
- The transporter then adds relevant details to the form and retains one copy (2), before transferring the remainder of the form, together with custody of the waste, to the next party (the off-site treatment/final disposal facility).
- The off-site waste disposal facility adds the final disposal details to the form and retains one copy (3).
- The remaining two copies are passed to the government regulator (4) and the generator of the waste (5).

The government regulator typically requires that copies of all documents be maintained in an auditable form by those that hold them, and may specify a minimum document retention period.
The generator records on the form information that is pertinent to the safe handling, treatment and disposal of the waste, including to whom and where the waste is being transferred. The facility receiving the waste will confirm acceptance and facility location, along with the manner of recycle/treatment/disposal applied, and will also confirm the type and quantities of the waste received. The waste record may also typically reference other relevant forms, such as safety information relevant to substances contained in the waste, or records of analyses that are important to those who require health and safety information regarding handling of the material, and those that require comprehensive information on the recycling, treatment or disposal of the waste.

Each transporter will insert their company details and contact information on the waste record, and will confirm the quantities handled. The waste generator should maintain a log of all wastes produced and transferred for recycling, treatment or disposal. In its simplest form the log can consist of a hard copy file containing the retained copies of the waste transfer documents themselves; alternatively, the information can be entered into an electronic database. The log can be updated as information confirming transfer and final disposition is received from the other parties in the waste management chain. A waste log can also be used to record waste types and quantities in on-site storage, which can be useful information to help safely manage the storage of wastes with potentially hazardous properties. A waste log can also provide a permanent record of on-site recycling/treatment/disposal, for due diligence and any government regulatory reporting.
All waste streams should be evaluated, as described in the sections above, for waste minimization opportunities (reduction, reuse or recycling). However, after those opportunities have been exploited, a waste stream will typically be managed on-site or off-site through a combination of storage, treatment and disposal methods as described below.

For wastes intended to be managed on-site at the refinery, waste handling and equipment operating procedures should be developed and documented. This will help to ensure compliance with any applicable legislation, and to minimize the risks of exposure of personnel to hazardous substances and the potential for contamination of soil and groundwater.

General recommendations include:
- Ensure any on-site handling, weathering or other treatment of wastes is performed only in designated areas and where equipment and procedures are in place to limit or control employee exposures to acceptable levels.
- Consider the potential to contaminate soil and groundwater when designing and operating any waste handling or treatment facilities, on-site pits and ponds or other waste storage areas.
- Monitor any on-site waste handling, storage, treatment and disposal operations to identify and prevent any potential contamination of soil and groundwater.

**Storage**

Storage requirements for wastes may be defined in national or local laws and regulations.

Storage of waste materials for periods of up to one year is considered short-term; however there may be regulatory definitions that define the period differently. Short-term storage is used to accumulate quantities of waste material that are more economically recycled, treated or disposed of when transported as full vehicle loads, or to allow for recycling, treatment or disposal in operations that operate intermittently. Short-term storage can take place in tanks, drums, skips, sacks or piles, depending on the waste material.

Waste storage areas should generally be designated as such in the facility waste management system, and should be indicated on a facility layout drawing. Their capacity, waste types to be stored, and operating practices should also be described. Access to waste storage areas should be controlled and documented to the extent that is necessary to: (a) allow for an inventory of wastes to be completed as required; (b) to avoid uncontrolled accumulation of wastes in the facility; and (c) to avoid tampering and unnecessary human or environmental exposure. Records of waste transfers into and out of storage areas should be kept in the refinery’s waste log.

Containers used to store waste should be suitable for purpose and compatible with the wastes to be stored; for example, it is essential that the waste does not react with, or pressurize, the container to the extent that its structural integrity may be compromised. Containers storing waste that would contaminate the soil or groundwater if spilled due to damage should be stored on impermeable surfaces.

Short-term storage of waste should take into consideration the next step in the life cycle of the waste to eliminate double handling of the material, where possible. Storage containers in which the waste can also be managed during treatment or disposal are ideal. Storing wastes in bulk, where possible, is preferable to using smaller containers because it can reduce or eliminate the need for handling, and also avoid the need to dispose of, or reclaim, the waste containers afterwards.

When waste is stored in piles, consideration should be given to having an ‘engineered’ waste
management area with impermeable hardstand areas or concrete pads. Piled waste storage makes it easier to handle the waste using equipment such as front-end loaders, while storage of piled waste on a concrete pad allows the waste material to be handled without the risk of it becoming contaminated with soil; this could increase the volume of waste for disposal and potentially lead to the treatment or disposal methods being less effective. Engineered storage areas should be designed to prevent contamination of soil within the immediate and/or adjacent areas with contaminants that may leach from the waste. An engineered storage area can also incorporate bunding and run-off collection to prevent contamination of stormwater or soil adjacent to the storage area. If contamination of the soil does occur due to spilled hazardous waste, the contaminated soil should itself be treated as hazardous waste (or as per host country regulations).

Stored waste should be kept covered when waste is not being added to the storage container. This prevents dust and other emissions to air (including potentially hazardous emissions and odours) from having an impact on areas inside the refinery or on neighbouring properties. Wastes should not be stored near drains unless suitable secondary containment precautions (e.g. a sluice gate) are in place to prevent spills from reaching the drains.

Stored waste should be identified with clear labels and signage that describe the type of material being stored. This should provide adequate hazard communication to personnel that will be responsible for handling or managing the waste. Labelling typically includes the chemical names of the material, the type of waste (hazardous or non-hazardous), the date that storage of the material commenced, and communication of all hazards appropriate to the waste in question. Labels should be attached to each container at an easily visible location, and should be sufficiently durable that they are able to remain legible for the period during which they will be required.

A log of the waste stored in each container should be kept in case any of the labels or markings fade due to sunlight, are washed off by rain, or become unreadable for any other reason. Marking each waste container using a wax crayon will create a permanent identifier which can then be recorded in the log to ensure the contents of the waste container are traceable.

Mixing different types of stored wastes should generally be avoided. When wastes are mixed, they typically need to be managed according to the characterization of the more hazardous material. Chemically or physically incompatible wastes should not be stored in the same location.

When long-term storage of waste is required, e.g. due to the lack of suitable recycling, treatment or disposal facilities, the storage facility should examine the stored waste at an established frequency, e.g. annually or every two years. Specifically, the location of the waste containers should be reconfirmed, and the condition of containers and labelling should be examined to ensure that they remain suitable for long-term storage. At the same time, the storage facility should ensure that the stored waste remains compliant with any applicable regulatory requirements relating to long-term storage of waste materials. The facility should also revisit
those processes that generate intractable wastes that have no local recycling, treatment or disposal options, with a view to eliminating or minimizing the production of such wastes.

Waste treatment

Waste treatment can be undertaken to decrease the mass or flow rate of the waste, or improve its characteristics (e.g. reduce its hazardous properties) or to enable the waste to be recycled or disposed of more safely, and in some cases to reduce disposal costs. Treatment requirements for wastes may be defined in national or local laws and regulations.

Treatment techniques typically used in relation to refinery waste streams can involve physical, chemical or biological processes; these are described below.

Physical treatment of refinery wastes

Physical treatment processes typically used on refinery wastes include the following:

- **In-line filtering**: a process for increasing the solids content of a waste stream and reducing water content. This can be less effective for treating oil, which tends to bind to, and clog, the filter material. Filters should then be wasted. Setting up a filter system that leaves most of the oil in the filter sludge increases the heat content of the waste filters; this is an important consideration if incineration is the ultimate disposal method.

- **Filter presses**: a process typically applied to sludge for dewatering purposes to reduce waste transportation costs. Separation of liquids into phases following filtering is often possible once the stabilizing solids have been removed. Calcium carbonate sludge can be a useful filter aid when oily sludge is being processed in a filter press. As with in-line filtering, setting up a filter press system that leaves most of the oil on the sludge side will increase the heat content of the waste, an important consideration if incineration is the ultimate disposal method.

- **Belt filter presses**: these are often used for dewatering secondary effluent treatment sludges that have higher water content and low oil concentrations. The feed is typically mixed with a flocculant or filter aid prior to being pumped onto the filter belt.

- **Centrifuges**: decanter centrifuges with a horizontal scroll are typically used for refinery sludge with oil contents of 10% or greater and solids content of up to 25%. Having a continuous, well homogenized feed of sludge is an important operating consideration.

- **Hydrocyclones**: these are useful in the separation of large volumes of oil and water where space for treatment is limited or the oil quantity is high. They are also useful in separating catalyst particles from support material, such as sand or clay.

- **Drying beds**: these are used to remove the last remains of water from sludge, or for treating a sludge that is not suited to another form of treatment. Drying beds can be operated at atmospheric conditions, or have heat applied to them, often in the form of steam coils.

- **Sludge dryers**: these are batch operated drum designs to which heat is applied and in which the sludge is turned over until it is dry. Vapour from the drying sludge is also often collected for treatment. Beds should be designed for easy application and removal of sludge.

Chemical treatment of refinery wastes

Chemical processes that are often used to pre-treat wastes include the following:

- **Solidification/chemical fixation**: a process for making material handling easier by transforming it from a fluid or semi-solid state into a solid state through the addition of material that binds the waste together or chemically fixes itself to the waste, resulting in a more easily managed material.
Stabilization: the conversion of waste to a chemically stable form of material that will resist leaching of contaminants from that material when it is placed in a landfill. Stabilization is often achieved by the addition of material which significantly changes the pH of the waste, followed by mixing to form pellets or a monolith of stabilized waste.

Encapsulation: this process involves the addition of a material that will coat the waste and bind to itself to completely enclose the waste within an impermeable layer of the encapsulating material. This process is often completed using cement to form monoliths of encapsulated waste that are then sent to landfill.

Biological treatment of refinery wastes

Biological treatment of refinery waste uses microbial action to convert hydrocarbons into carbon dioxide and water at higher rates than would otherwise occur naturally. Bioremediation or biocomposting can be applicable to certain refinery wastes, particularly oil-impacted soils. The ability to use these techniques will depend on the content of oil that can be metabolized by bacteria, and on whether the waste contains concentrations of any other substances that can poison or slow down the biological reactions. All of the biological treatment options use naturally occurring soil bacteria to break down organic wastes under carefully controlled conditions.

This type of biological treatment is fundamentally driven by two factors: it is completed in the liquid phase (where the bacteria live) but it is significantly dependent on gas to liquid phase oxygen transfer rates. Important parameters for successful biological degradation of waste materials include: oil content; oxygen transfer; moisture content; pH; temperature; and trace nutrient concentrations.

Use of biological treatment methods can require significant space for treatment and storage of material, and may require regulatory approval or a specific permit to carry out this type of treatment.

It is also possible to biologically treat some liquid-phase wastes in tank-based processes that can operate either aerobically or anaerobically. A detailed description of these waste treatment processes is outside the scope of this document.

Waste disposal

Final disposal is meant to be a permanent repository for the waste from which it is not expected to return or be moved. It is typically the responsibility of the generator of a waste to ensure that the final disposal method selected is safe and will not result in adverse impacts on the environment.

Petroleum refinery waste materials can ultimately be disposed of in the following ways:

- landfill;
- incineration; and
- deep well injection.

Landfill

Landfills can exist on-site or off-site. They are typically classified by the type of waste that they can accept, such as municipal waste, construction waste, hazardous waste or industrial non-hazardous waste. It is typical to use off-site landfills for final disposal of refinery waste streams, but in some cases a landfill may be located inside the refinery perimeter, for example if no safe or environmentally suitable options exist elsewhere.

Landfills are facilities specifically designed and engineered to contain the waste and prevent migration of the waste or any associated contaminants into the surrounding soil or groundwater. For landfills intended to contain
wastes with leachable components, this is achieved by lining the base and sides of the landfill with an impermeable membrane and, where possible, locating the landfill within an impermeable geology (e.g. clay, non-fissured rock). To minimize water ingress, non-operating areas of the landfill may be capped with an impermeable layer, and surface water run-off from neighbouring land is diverted away from the landfill. Within the landfill, any water present (leachate) is contained or treated prior to discharge. Where the landfill also accepts biodegradable material, collection systems to capture and use or safely dispose of methane gas produced as the material decomposes in the landfill may be present.

**Incineration**

Waste incineration can be completed on-site or off-site. For the purposes of this guidance, incineration is considered to be any process that combusts waste material in the presence of oxygen, with or without energy recovery. Refinery wastes with a high content of hydrocarbons, or flammable wastes can also provide a significant portion of the fuel requirement for an incinerator. Waste incinerators can also be the source of significant heat and energy recovery opportunities.

Incinerators are controlled by varying the amount of combustion air, temperature of combustion, residence time and mixing to carry out effective combustion. Incinerators come in many designs, each type of which is best suited to the disposal of specific types of wastes based on the parameters above.

All incinerators generate solid ash and air emissions. All incinerators should have some form of air pollution control and a means of monitoring the performance of the combustion process, and pollution control equipment to verify that they comply with regulations and permits held by the operator. During the waste characterization process, the concentrations of metalloids in ashes, such as As, Se and Hg, should be quantified in order to verify the limiting concentration for incineration, following standard laboratory procedures e.g. EPA SW 846.

**Deep well injection**

Injection of waste materials to deep formations through wells has historically been allowed in a number of locations. This method of ultimate disposal uses injection wells to place treated or untreated liquid waste into deep geologic formations that demonstrate no potential for migration of contaminants into potential potable water aquifers. A typical injection well would be drilled to more than 1000 m depth into a non-potable, permeable injection zone that is confined vertically by impermeable rock. The outermost casing of the well would be installed to extend below the base of any underground sources of drinking water and would be cemented back to the surface to prevent contamination of any useful aquifer.

While deep well injection is a possible route for disposal of some petroleum refinery waste materials, its use is currently limited due to perceived risk and long-term liability. Disposal by deep well injection should not be a preferred option in most cases and only used if all other options have been thoroughly reviewed. For existing deep injection wells, use should be defined on the basis of the holistic risk on a short- and long-term basis.
Risk management and economics will largely determine the amount of on-site treatment and recycling, as well as the construction and use of any on-site disposal facilities. Key considerations when planning such facilities include:

- the facility’s location in relation to other adjacent properties, population centres and environmentally sensitive areas;
- assessment of the site conditions, location, topography, land-use, soil quality, hydrogeology, etc.;
- the expected lifetime of the facility;
- the possible future uses of the site;
- the need for regulatory agency permitting of treatment or disposal facilities; and
- management of the facility both during its operation and following closure to minimize potential current or future risks to the environment.

In many countries, government environmental, health and safety regulators require that all new facilities inside a petroleum refinery boundary, as well as significant changes to existing facilities, obtain a permit or licence to build and/or operate them. This process is generally referred to as ‘permitting’. A single authority or multiple regulatory authorities may be involved in the permitting process, depending on the location. Permitting may be handled at the local, regional or national level, so research into the regulatory framework that applies to a particular refinery should be completed early in the process of determining whether or not waste treatment or disposal facilities are to be added. Permitting of a new waste management process at a refinery may be a relatively straightforward activity, or it may be extremely complex, time-consuming and costly, depending on the nature of the planned facilities and the existing regulatory framework. The cost of permitting should be factored into the cost of treatment or disposal facilities when comparing options, and the time required for the permitting process should be factored into the project schedule early to avoid delays in projects and possible additional cost associated with delays.

Planning for monitoring of the soil and groundwater at a refinery that intends to carry out waste disposal on-site should consider the installation or expansion of the monitoring capabilities at the site. This will ensure that there is a means to establish the baseline condition of the soil and groundwater, as well as facilitate routine sampling of the conditions as time goes on to ensure that contamination is not occurring as a result of the waste disposal.

If on-site landfills are used, care should be taken to ensure appropriate construction. The use of a detailed three-dimensional record-keeping system is recommended to track the precise locations at which specific waste streams are placed, to adequately manage future liability issues that may arise.

When evaluating on-site waste facility installation, the costs involved in the eventual shutdown and clean-up of these facilities according to local government environment, health and safety standards need to be considered. Where significant closure activities are required, the additional closure activities required for well-designed and operated waste treatment and disposal facilities at a refinery are unlikely to represent a significant additional burden; however, on-site waste management facilities, in particular landfills, can require long-term care, monitoring and maintenance commitments.

It is important to note that government authorities may require closure activities to begin when a waste management activity is discontinued at a site, even if the rest of the refinery operations continue to operate. In particular, this would apply to landfills that are filled to capacity and closed.
Off-site treatment and disposal contractor issues

Most petroleum refineries use contractors to manage the transport, recovery, recycling, treatment or disposal of waste at third-party facilities off-site. The selection of contractors should include a validation that the contractor holds appropriate licences for its activities, and can fulfil their obligations for documentation of chain-of-custody transfers as well as addressing any environmental, health and safety risk posed by the waste material. An inspection of all contract facilities that carry out waste treatment or disposal is recommended (see the following section on Waste site assessment and audit.)

Contract documentation should require that appropriate licences are held for the activity, and should clearly communicate chain-of-custody transfers that take place. The petroleum refinery should also ensure that all appropriate waste transfer documentation is produced and retained for all wastes sent for off-site waste management in line with its waste management system.

Off-site disposal of waste to landfill is a widely used option for final disposal of many wastes where no other option higher on the minimization hierarchy is practical or economically feasible. Refineries that are located where no acceptable landfill facilities are available for use may choose to form consortiums with other industrial and commercial facilities, and with the government, to establish or improve facilities to a suitable standard.

Transport contractors are also widely used by petroleum refineries to transport wastes to recycling, treatment and disposal facilities. The selection of transport contractors should also include verification that the transport contractor holds appropriate licences for its activities, and can fulfil their obligations for documentation of chain-of-custody transfers and manage any environmental, health and safety hazards of the waste during transport. This includes safe containment, signage, spill prevention and control preparedness, vehicle and driver competency requirements and training.

Contractor facilities and their performance should be inspected periodically, at regular intervals or as contracts are amended or renewed. Assessment of contractor facilities is covered in the following section on Waste site assessment and audit.
Waste site assessment and audit

To ensure waste management is being carried out appropriately on an ongoing basis, the refinery should consider undertaking operational audits of waste management facilities and activities both on-site at the refinery and at off-site locations managed by waste contractors. Audits should be conducted at regular intervals and/or as contracts are amended or renewed in the presence of treatment process experts. Environment and safety experts should follow the process as well, in order to ensure the verification of technical aspects of good practices, environmental aspects of the process, and worker and installation safety. Audits carried out on waste management activities should focus on ensuring that systems are in place to ensure safe and environmentally responsible waste management (organization, procedures, equipment, record keeping and regulatory compliance) and to evaluate the level of performance being delivered.

Audits of contracted waste management facilities to be used by a petroleum refinery should, at a minimum, include an assessment of the following key elements:

- facility contact details including address, ownership and key management contact details;
- types of waste accepted and rates of those wastes currently processed;
- verification that the treatment/disposal methods used are appropriate for the types of waste accepted;
- verification that all required regulatory permits are in place and that the facility is in compliance with them;
- location of the facility in relation to sensitive receptors (e.g. local population centres, surface waters, wildlife habitat, drinking water aquifers, groundwater abstraction wells);
- how the facility is designed and operated to provide environmental protection;
- site safety practices, procedures and training;
- the ability to respond to incidents, (response plan, procedures, training);
- materials storage and handling practices and equipment used;
- details of any processes used for recycling, treatment or disposal, including how any emissions from these processes are treated/managed to minimize impacts on the environment;
- effectiveness of emission monitoring and controls;
- evidence of enforcement action by regulatory authorities and how the site has responded;
- verification of the demonstration of financial stability with regard to site closure and post-closure monitoring, and of relevant insurance held;
- details of any soil or groundwater impacts from current or historic operations at the site;
- site security, particularly with regard to the prevention of unauthorized access to the facilities; and
- history of relations between the facility and its neighbours.
Crude oil desalting

Following acceptance and storage, the first process applied at every refinery is the desalting of crude oil, which protects costly refinery equipment from a variety of substances such as inorganic salts (chlorides of sodium, magnesium and calcium), water-soluble trace metals and other suspended solids contained in the crude oil. These substances cause corrosion, plugging and fouling of equipment, and deactivate the catalysts in downstream processing units.

The desalting process is designed to remove the contaminants that are dissolved in the water that is present in the crude oil, not in the crude oil itself. The water that is present in crude oil is the remaining produced water from the formation where the crude was extracted, along with water that is also used in the transfer of crude oil from its source to the refinery location. Desalting involves the mixing of heated crude oil with water (about 3–10% of the crude oil volume) to extract the soluble contaminants. To ensure thorough extraction, the desalter should achieve intimate mixing of the water and crude oil.

Heating of the crude oil (to a temperature of between 65–175°C) allows easier mixing and separation of the water, as it reduces viscosity and surface tension. A desalter operates at pressures of at least 275 kPa. The intimate mixing is achieved when water and crude oil are passed through the emulsifier orifice. Then the oil-water emulsion is introduced into the gravity settler.

The two most typical methods of crude oil desalting are chemical and electrostatic separation, which are conducted in multiple stages to increase desalting efficiency. In chemical desalting, water and a chemical surfactant (demulsifier) are added to the crude, heated so that salts and other impurities dissolve into the water phase, and then passed to a gravity settler. Electrostatic desalting is the application of high-voltage electrostatic charges across the gravity settler to agglomerate water droplets at the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids. Both methods of desalting operate as continuous flow prior to the distillation unit, often in parallel.

Figure 6 Electrostatic desalting flow diagram
Following separation in the gravity settler, two waste streams are generated and settle at the bottom of the gravity settler: an oily sludge, which continuously builds up as crude is processed; and a high temperature salt-water stream that is removed continuously.

‘Mud washing’ is used to remove the sludge from the gravity settler on a regular basis. During mud washing, the desalter is diverted to tankage, and water jets are used to scour the sludge from the gravity separator drum and flush it out of the unit to other tankage (such as slop tanks), processing/hydrocarbon recovery units or the wastewater treatment plant. Desalter sludge removal may result in sludge/sediment build-up in the downstream receiving tankage or units, with corresponding loss of residence time in those units, so consideration should be given to potential impacts on slop or other intermediate stream quality resulting from the increased sediment load.

In some cases, desalting sludge is removed once every several years during unit turnaround and inspections (T&I), often with the associated distillation column. At these times, sludge is removed from the desalter using vacuum trucks, permanent or portable piping. Sludge is scoured from the unit with water, and can be centrifuged prior to disposal. In fewer cases maintenance workers remove it manually. Desalter sludge is typically transferred to the refinery wastewater treatment plant, transferred for use as a fuel on-site, dewatered and sent to landfill, or in fewer cases incinerated or sent for land treatment.

**Good practices for minimizing desalter waste**

- Using chemical demulsifiers and electrostatic precipitation to reduce the volume of desalting sludge and improve separation.
- Shear mixing of desalter wash water and crude to reduce water volume required.
- Reducing turbulence in the desalter by using lower pressure water to prevent emulsion formation and better separation.
- Replace water jets with mud rakes to remove solids to reduce turbulence.
- Sludge dewatering to reduce the intermediate storage required.

Waste disposal from desalter units applies to the sludge produced, since the wastewater stream is typically sent to the refinery wastewater treatment plant. Where it does not interfere with the refinery process, wastewater sewer system or treatment plant, desalter sludge can be washed out periodically and disposed of to the sewer. Where desalter sludge is removed in batches, hazardous materials that can be present should be considered in treatment and disposal.

After being treated in a desalter, the crude is subjected to initial distillation. Distillation involves separation of more volatile materials from less volatile materials through the processes of vaporization and condensation. Petroleum refineries employ distillation at atmospheric pressures, and vacuum distillation at pressures lower than atmospheric pressure. Lighter end products (naphtha, gasoline, kerosene, light fuel oil, diesel oils, gas oil and lube distillate) are separated in atmospheric distillation units. The heavier fractions from atmospheric distillation that cannot be distilled without cracking under its pressure are sent to vacuum distillation units or thermal treatment.

Typically, little or no solid waste is generated during distillation. The main waste streams are air emissions produced from the combustion of fuels in the furnaces to heat the crude oil, sour/acid gas from the distillation column that is sent to a refinery sour gas treatment system, and oily sour water (condensed steam containing hydrogen sulphate and ammonia) that is treated in the refinery wastewater treatment plant. Sludge or scale from periodic distillation column turnaround and inspection is managed with similar materials, typically to landfill or thermal treatment.
Catalytic cracking

Catalytic cracking is a chemical conversion process that converts heavy complex hydrocarbons from the atmospheric distillation process into lighter, more valuable products and reduces the amount of heavy residuals. The efficiency of cracking and the end products are dependent on the temperature and catalyst used.

Three types of catalytic cracking processes are used in refineries. These are: fluidized catalytic cracking (FCC); moving-bed catalytic cracking; and Thermofor® catalytic cracking (TCC). The most prevalent of these is fluidized catalytic cracking, where a catalyst and gas-oil feed are contacted in a fluidized bed where the reaction takes place. The FCC process is shown in Figure 7.

In the FCC process, a preheated hydrocarbon charge is mixed with hot, regenerated catalyst as it enters the riser leading to the reactor. The feed is vaporized and raised to reactor temperature (480–530°C) by the hot catalyst as it travels up the riser. As the mixture travels up the riser, it begins to crack at low pressure (70–200 kPa). The cracking continues until the oil vapours are separated from the catalyst in the reactor cyclones. The resultant product stream (cracked product) then goes to a fractionating column where it is separated into fractions that undergo further processing or are blended into products. The clarified slurry oil (CSO) from the bottom of the fractionator is recycled to feed stream in the riser, or blended into fuel products such as No. 6 fuel oil.

Zeolite, bauxite, silica-alumina, and aluminium hydrosilicate are all catalysts commonly used in FCC units. Spent catalyst and catalyst fines from air pollution control devices (such as electrostatic precipitators) are the primary solid waste from an FCC unit. These are typically sent

Figure 7 Fluidized catalytic cracking flow diagram
to landfills or to reuse/recycle outlets such as cement kilns as raw material for use in the cement manufacturing process. Sludge (which includes catalyst fines) from the slurry settler and from the bottom of tanks is also removed and disposed of during turnaround and inspection.

**Good practices to consider for minimizing catalytic cracking waste**

- Use higher efficiency cyclones to minimize the amount of fines that escape from the reactor with the overhead product and leave the unit entrained in decant (slurry) oil.
- Solids reduction of storage tank influent through the use of mechanical filtering, or use of a hydrocyclone, slurry settler or similar device to remove the solids (catalysts fines) in the slurry oil. These devices can remove more than 80% of the solids, which are then recycled back to the FCC unit.
- Substitution of spent catalysts for fine aggregate (sand) in cement mortars.
- Catalysts in the decant oil can be minimized by using a decant oil catalyst removal system. It incorporates high voltage electrostatic fields to polarize and capture catalyst particles in the oil.
- Minimize spillage of catalyst and catalyst fines to prevent carryover to the wastewater treatment facilities.

Spent catalysts from FCC units may not be hazardous if they have been de-coked and steam stripped prior to removal from the system. It is advisable to have the spent catalyst tested by the catalyst supplier to determine metal content as this can affect the disposal method and the usefulness of the spent catalyst.

Leachate testing of spent catalyst can confirm whether it can be disposed of as normal (non-hazardous) industrial waste.

Sludge from slurry oil tanks may be managed along with other tank sludge, or managed separately depending on hazardous characterization. It may be able to be processed in a refinery coker, or there may be opportunities to use it for its fuel and/or raw material value (such as in cement kilns). If reuse opportunities are not available, it can be managed by methods such as thermal treatment or incineration.

**Catalytic hydrocracking**

Hydrocracking is used to remove organic sulphur, nitrogen, and metals and to saturate olefins and aromatics from those fractions that cannot be cracked effectively in catalytic cracking units. The feedstocks include middle distillates, cycle oils, residual fuel oils, and reduced crude.

Catalytic hydrocracking normally utilizes a fixed-bed catalytic cracking reactor with cracking occurring under substantial pressure (8.2 to 13.5 MPa), high temperature, catalyst and in the presence of hydrogen. It is a two-stage process typically carried out in a two-stage reactor. In the first stage, the feed is mixed with hydrogen-rich gas pumped to operating pressure, heated and fed across a catalyst bed, where sulphur and nitrogen are converted to hydrogen sulphide and ammonia. In the second stage, saturation of olefins and cracking of heavy aromatics to form lighter compounds occurs. Following hydrocracking, the product stream is stabilized and fractionated. Figure 8 provides an example of the hydrocracking process. The hydrotreating process, used on a number of streams in refineries, is similar to hydrocracking but is operated at significantly lower pressures, where treatment of the hydrocarbon streams to remove contaminants only is required and the hydrocarbon molecules are not decomposed (cracked).

Catalysts employed in hydrocracking reactors are dual-functional. They consist of a metallic component (cobalt, nickel, tungsten, vanadium,
molybdenum, platinum, palladium or a combination of metals) supported on a highly acidic substrate (silica-alumina, acid-treated clay, alumina). The metallic component catalyses the hydrogenation and desulphurization/denitrification reactions and the acidic component catalyses the cracking reactions. In addition, heavy metal contaminants are adsorbed onto the catalyst, causing them to be deactivated over time to the point where they must be changed out.

Hydrocracking and hydrotreating catalysts become deactivated and have to be changed every 6 months to 8 years depending on cracking severity and the type of catalyst used. Prior to removal, the catalyst is typically swept with hydrogen and then nitrogen, or steam. The catalyst is then removed from the reactor vessels by being dumped or water drilled. After removal from the reactor vessel, the material may be screened to remove fines or the catalyst support media. Waste hydrocracking catalyst is typically shipped off-site for disposal or recovery.

**Good practices for minimizing catalytic hydrocracking waste**

- To reduce the frequency of catalyst changeout, base-metal catalysts rather than noble-metal catalysts can be considered as they are more resilient and can process much more difficult feed blends while compensating for any feed upsets. However, base-metal systems may have lower production yields.
- Increasing catalyst life through the use of contaminant inhibitors, such as treatment of silica in naphtha feed streams.
- Use of guard beds with on-stream catalyst replacement prior to hydrocracking.
- Spent catalysts can sometimes be recovered in-situ (e.g. oxygen burn).
• Cascading reuse of the catalysts to another process unit (hydrotreater) that requires lower activity.
• Regeneration, reclamation, or other use off-site for spent catalysts such as incorporation of alumina-based catalysts in cement kilns that require trace metals in their feed.
• Use of volume reduction techniques, such as screening.

Often the catalyst is suitable for recovery and regeneration. However, where hydrocracking catalyst is to be disposed of, it is typically sent to landfill. It is appropriate to test the spent catalyst to determine if the level of the contaminants may result in it being classified as hazardous. This testing will determine the type of handling and disposal required for the spent catalyst.

Catalytic reforming

Catalytic reforming is used to convert naphthas typically with low octane ratings to high-octane products (called reformate), which are components of high-octane gasoline. There are many different commercial catalytic reforming processes including platforming, powerforming, ultraforming, and Thermofo® catalytic reforming.

The platforming process (named after the terms platinum and reforming) uses a small amount of platinum as an active catalyst. Sometimes platinum catalyst is combined with a second catalyst (bimetallic catalyst) such as rhenium or another noble metal. A catalytic platforming process comprises a reactor section containing three reactors with fixed-bed catalyst and a

**Figure 9 Schematic of a catalytic platforming unit**
product-recovery section as shown in Figure 9. Platforming is carried out at temperatures in the range of 450–525°C and pressure in the range of 1520–7100 kPa.

Before going to the platformer, the naphtha feedstock typically undergoes hydrotreatment and distillation to remove impurities, thereby reducing catalyst degradation. The naphtha feedstock is then mixed with hydrogen, vaporized, and passed through a series of alternating furnace and fixed-bed reactors containing the catalyst. In the process, hydrogen is separated from the hydrocarbon, which results in a significant amount of hydrogen gas being produced as a by-product, which can be used in a number of refining processes. The hydrogen also prevents a rapid build-up of carbonaceous material on the catalyst.

The overhead product from the fractionator contains methane, ethane, propane and butane gases, produced as by-products by the hydrocracking reactions that also occur in the reactors. This gas stream is routed to the refinery’s central gas processing plant for removal and recovery of the propane and butane.

The catalyst is regenerated in-situ during routine catalyst regeneration shutdowns, which occur every 6 to 24 months. In some refineries one reactor at a time is taken off-stream for catalyst regeneration.

**Good practices for minimizing catalytic reforming waste**

- Use of continuous catalyst regeneration reformers (CCR), which allows for continuous regeneration of catalyst in-situ and recycle of the catalyst to the reactors.

When reforming catalyst loses its activity, it is typically sent off-site for the recovery of precious metals.

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**Isomerization**

Isomerization processes are used to alter the arrangement of a molecule without adding or removing anything from the original molecule. It is used in refineries to increase the production of high octane, low aromatic gasoline. Isomerization is important for the conversion of n-butane to isobutane to provide additional feedstock for alkylation units, and in the conversion of naphtha (pentanes and hexanes) into more highly branched isomers for gasoline blending. A distinct process is used for each type of isomerization, although both processes use the same type of catalyst, typically platinum or platinum chloride on an alumina or zeolite substrate.

**Butane isomerization**

The n-butane feedstock is generated throughout a refinery and separated from other butanes by distillation. Butane isomerization is carried out at temperatures of 110–175°C and pressures of 1,375–2,000 kPa. The feedstock is combined with hydrogen and a chlorinated organic solvent. The hydrogen is used to suppress the polymerization of olefin intermediates, while chlorine source is used to maintain catalyst activity. Following the reactor, hydrogen is then flashed off in a high-pressure separator and hydrogen chloride removed in a stripper column. The resultant butane mixture is sent to a fractionator (deisobutanizer) to separate n-butane from the isobutane product. A process flow for butane isomerization is shown in Figure 10.

The platinum chloride catalyst is susceptible to deactivation by nitrogen, sulphur and water. The feedstock is generally desulphurized prior to the isomerization process, and treating clays or adsorbents (mostly molecular sieve) are used for drying desulphurized feedstock, producing waste during change-out.
**Naphtha isomerization**

The naphtha feedstock is most commonly sourced from atmospheric crude oil distillation. First, the feedstock is pretreated to remove any water, and combined with hydrogen and an organic chloride before being passed over the supported-metal catalyst in the first reactor where benzene and olefins are hydrogenated. The feed then goes to the isomerization reactor where the paraffins are catalytically isomerized to isoparaffins. The reactor effluent is then cooled and subsequently separated in a flash separator into a liquid product (isomerate) and a hydrogen-gas stream that can be recycled. The isomerate is washed (caustic and water), acid stripped and neutralized before going to storage. A process flow for naphtha isomerization is shown in Figure 11.

As with butane isomerization, the platinum chloride catalyst is susceptible to deactivation by water, sulphur and nitrogen. Hydrodesulphurization and guard columns utilizing zinc oxide, nickel on alumina or copper oxide are used to protect against sulphur contamination. Molecular sieves are also typically used for drying desulphurized naphtha feedstock.

When it becomes necessary to replace the isomerization catalysts, they are almost always sent off-site for recovery, due to their precious metal content. Molecular sieve material loses its capacity or efficiency and is replaced approximately every five years. Calcium chloride sludge is also produced from acid neutralization of the naphtha isomerate. Spent catalyst and adsorbents from isomerization are vacuumed or gravity dumped from the reactors/vessels and typically sent off-site for recovery or landfilled.
**Good practices for minimizing isomerization waste**

- Increase the life of the catalyst by removing catalyst contaminants from the feed, such as H₂S and water prior to introduction to the reactor.
- Consider the addition of materials such as erionite to the platinum catalyst to increase isomerization.
- Reuse the isomerization treating clay at a cement plant or for mixing with road base material.

When disposed as waste to landfill, facilities should take into consideration the hazardous components that may be present in the waste isomerization catalyst. Because this catalyst is regularly treated in process with an organic chloride chemical, health and safety considerations are of utmost importance in the processing and long-term disposal of any material containing organic chloride residue. If not recovered safely at a recycling facility, this material should be disposed of as hazardous material, unless it can be demonstrated otherwise through characterization studies.

**Solvent extraction**

Solvent extraction can be frequently used in a refinery. It is used to remove aromatic impurities from hydrocarbon streams in the manufacture of lubricants. Solvent extraction is also used in various locations to remove contaminants such as: organic compounds containing sulphur, nitrogen and oxygen; inorganic salts and dissolved metals; and soluble salts that were present in the crude feedstock.
In a generic process, like the one shown in Figure 12, the solvent will run counter current to the stream being treated. The solvent containing the extracted material will be run through a stripper column to return the solvent to the process and release the extracted material for beneficial use or disposal, depending on whether it is a contaminant (salts, metals) or a valuable material (raffinate, aromatics, sulphur). The most common extraction solvents are furfural, phenol and cresylic acid, sulfolane (C4H8SO2) or tetraethylene glycol.

Another type of solvent extraction, called dewaxing, uses a solvent blend to extract solvent-soluble wax from a hydrocarbon stream. Typically, a mixture of solvents is used, such as toluene (that dissolves oil and wax and maintains fluidity at cold temperatures), and methyl ethyl ketone (MEK), to precipitate the wax at low temperatures. The solvent blend is mixed with the feedstock, chilled to precipitate wax, and then the solvent is recovered from the wax through a combination of distillation and steam stripping.

All types of solvent extraction are closed processes that do not produce waste streams on a continuous basis. Treating clay can be used (as in the example above) to further purify valuable streams following solvent extraction, and when used, it produces intermittent waste filter clay. Extraction clays are generated more frequently and in greater quantity than isomerization clays.

**Good practices for minimizing solvent extraction waste**

- Reuse of extraction clays for off-site catalyst regeneration/metals reclamation, and reuse in cement plants.

Spent treatment clay from solvent extraction is typically sent to landfill. It should be characterized to identify hazardous components prior to disposal.
Alkylation

The alkylation reaction combines isobutane with light olefins in the presence of a strong sulphuric or hydrofluoric acid catalyst to produce a high-octane gasoline blending stock. The general chemistry of the sulphuric acid (H₂SO₄) and hydrofluoric (HF) acid alkylation processes are the same. However, the HF process includes a closed loop and integral recycling step for the HF acid, while the sulphuric acid process requires a separate acid regeneration process; this regeneration is typically carried out off-site by an external service provider.

Sulphuric acid alkylation process

In the sulphuric acid process, the olefin feedstock (propylene, butylene, amylene and fresh isobutane) is first cooled (the process runs best at temperatures of 4–10°C) and then enters the reactor and contacts the concentrated sulphuric acid catalyst to synthesize alkylates. The reactor effluent is separated into hydrocarbon and acid phases in an acid settler, where acid is drawn from the bottom and recycled back to the reactor. The hydrocarbons stream is drawn from the top of the settler and washed with caustic prior to being separated in a fractionating column. Isobutane is recycled to the reactor feed, and the other saturated gases may be treated with filter clay. The process is shown in Figure 13.

The recycled acid stream from the acid separator requires periodic or continuous purging and make-up acid to minimize impurity build-up and to maintain adequate acid strength at around 90%. The spent acid is stored for off-site for regeneration. Any acid carryover from caustic wash is discharged to a neutralization tank (or open pit). Pits are often used for final neutralization as they also serve as the spill and drainage control point for the entire alkylation process area.

Figure 13 H₂SO₄ alkylation process flow diagram
Typically, neutralizing agents (sodium, calcium, potassium hydroxides) are used to complete treatment in the tank or pit prior to discharge of the liquid material to the refinery wastewater treatment plant and management of any sludge of precipitated salts.

**Good practices for minimizing sulphuric acid alkylation process waste**

- Use of zeolite solid acid catalyst systems (e.g. AlkyClean®) to reduce the operating costs and sulphuric acid consumption.
- Use of alkylate to extract light hydrocarbons from the recycled acid stream followed by secondary separation to reduce light hydrocarbon entrained in the spent sulphuric acid.
- Decrease neutralization pit sludge generation by switching from insoluble neutralizing agents (e.g. lime) to soluble agents (sodium hydroxide).
- Use distillation as an alternative to molecular sieve to dry the feed for alkylation, to reduce the volume of waste.

**Hydrofluoric acid alkylation process**

Hydrofluoric acid (HF) alkylation is similar to the sulphuric acid alkylation process, except that in an HF alkylation unit, the HF catalyst is managed in a closed-loop process, never leaving the unit for replacement or regeneration. Olefin and isobutane gases are contacted over a hydrofluoric acid catalyst to synthesize alkylates. The reactor effluent is then separated in an acid settler. Hydrocarbons are drawn off the top of the settler and sent to a separator, where the alkylate product is removed. The acid is drawn from the bottom of the acid settler and recycled back to the reactor. A slipstream of acid from the recycle stream is drawn off continuously to an acid regenerator. The regenerator distills HF acid from other contaminants, producing an acid-soluble oil stream. HF acid from the regenerator is recycled back to the reactor. Fresh acid is added to replace acid losses daily. The HF alkylation process is shown in Figure 14.

**Figure 14 Hydrofluoric acid alkylation process flow diagram**
Light hydrocarbon overheads from the fractionator are processed in an alumina treater to be catalytically defluorinated, treated with potassium hydroxide and sent to LPG storage. Potassium hydroxide is depleted in the process and may be regenerated on-site or off-site by an external service provider.

The acid-soluble oil is decanted from the acid regenerator to produce an aqueous phase (azeotrope) and an acid-soluble oil product that is washed with potassium hydroxide and blended into fuel oil or used as fuel at the refinery. The azeotrope is neutralized in a tank or pit. As with sulphuric acid alkylation, this pit also serves as the drainage control and neutralization point before discharge to the refinery wastewater treatment plant. Calcium fluoride sludge is produced from this pit and should be managed as waste.

Molecular sieve materials are used to treat both types of alkylation feeds, on occasion, to remove water (reducing their use is mentioned as a waste minimization good practice, for both HF and H₂SO₄ alkylation). Light hydrocarbon overheads from HF alkylation are frequently also treated through alumina adsorbents, while sulphuric acid alkylation overheads are infrequently treated with filter clay adsorbents.

**Good practices for minimizing hydrofluoric acid alkylation process waste**

- Use the sulphuric acid alkylation process, where economically feasible, to reduce the risk of working with HF acid and alumina waste volumes.
- Use solid acid catalyst systems to eliminate neutralization sludges and reduce the volume of acid-soluble oil produced.
- Sending spent alumina to an aluminium smelter or a cement kiln to be used as process feeds.
- Using distillation as an alternative to molecular sieve to dry the feed for alkylation, to reduce the volume of waste.

External service providers can reclaim waste molecular sieve material and alumina adsorbents from HF alkylation. If the material is to be landfilled, it should be characterized for hazardous components prior to disposal. Insoluble calcium fluoride sludge is also typically sent to landfill.

Acid-soluble oil is a hazardous material due to its ignitability and the toxic constituents present in it. The material should be fully characterized if it is to be managed as a waste at either an on-site or off-site facility.

**Polymerization**

Polymerization is a conversion process where short-chain olefin streams from other processes are converted into polymer gasoline for blending into final fuel products. Two types of polymerization processes that are widely used are phosphoric acid polymerization and the Dimersol® process. With either process, the olefin feedstock is pre-treated to remove sulphur and water.

**Phosphoric acid polymerization**

In the phosphoric acid polymerization process, reactor feed is charged to a vessel with a header connected to many tubes filled with the catalyst. Cooling water is used in the shell side of the reactor to remove heat, as the reaction is highly exothermic. The reaction conditions are controlled to stop the polymerization at the desired C6 or C9 product. The reactor effluent is then fractionated to remove the products from any unreacted feed. The product is then stabilized to remove any light hydrocarbon gases before fuel blending. A process flow diagram for phosphoric acid polymerization is provided in Figure 15 on the following page.
Phosphoric acid polymerization catalyst becomes inactive over time and must be removed during turnaround and inspection of the facility.

**Good practices for minimizing phosphoric acid polymerization process waste**
- Process optimization to extend catalyst life.

Waste phosphoric acid catalyst is typically disposed of to landfill, but could be a good candidate for use in biological treatment processes as it can be a good source of phosphorus for biological treatment.

**Dimersol® polymerization**

In the Dimersol® process, the olefin feed is combined with a liquid nickel carboxylate/ethyl aluminium dichloride (EADC) catalyst prior to entering a three-stage reactor. The reactor feed is converted to product (called dimate) primarily in the first stage of the reactor, and additional conversion is achieved in the second and third stages of the reactor. The reactor recycle stream must be cooled, as it is highly exothermic. The final reactor effluent consists of dimate product, unreacted olefins and the liquid catalyst.

The liquid catalyst is removed from the reactor effluent by treating the reactor effluent with caustic, followed by water washing and filtering to remove solids. Spent caustic waste containing the catalyst is typically reused or reclaimed in the refinery or sent off-site for recycling by an external service provider. After filtering, light hydrocarbons are removed from the dimate in a stabilizer before product blending, similar to polymer gasoline. LPG from the stabilizer is sent to storage in the refinery. The Dimersol® process is shown in Figure 16.

Filters should be changed in the catalyst removal system and disposed of periodically. Some reactor sludge is produced during turnaround and inspection of the systems.
Good practices for minimizing polymerization process waste

- Process optimization to extend filter life and reduce caustic use.

Wastes from Dimersol® polymerization are sent to landfill or can be processed in a coker unit on-site.

Residual upgrading

Waste upgrading includes processes where asphalt components are separated from gas oil components by solvent extraction and where the asphalt value is upgraded by oxidation prior to sale. The feed for the residual upgrading processes consists of the vacuum distillation bottoms and other residuum feeds. There are four types of residual upgrading processes:

- solvent deasphalting;
- asphalt oxidation;
- supercritical extraction; and
- asphalt emulsion.

Solvent deasphalting

In solvent deasphalting residue is separated by the molecular type, instead of by boiling point as in the vacuum distillation process. The residue feedstock and hydrocarbon solvent are mixed and charged to the extractor under pressure. The types of solvents used depend on the type of the residual being processed and the use of products (e.g. propane for lube oil production, a mixture of propane and butane for preparing feedstocks for catalytic cracking, pentane for catalytic cracking or low sulphur fuel oil).

The extract contains the paraffinic fraction, called deasphalted oil (DAO), and the raffinate contains the asphaltic components. The extract and raffinate streams are sent to separate solvent recovery systems to reclaim the solvent for recycling back to the process. A process flow diagram for solvent deasphalting is provided in Figure 17.

Sludge from the process is disposed of as waste to landfill or incineration, or managed as reusable material through the refinery slop oil system. Off-spec product produced during process upsets can also often be recovered and returned to slop oil or processed in a refinery coking unit.
Asphalt oxidation (asphalt blowing)

Heavy gas oil from distillation and residuum from vacuum distillation can be upgraded by oxidation with air to produce higher quality asphalt products. Feed is heated in a pipestill almost to its flash point and charged to a blowing tower where hot air is injected for a predetermined time. Steam, used to blanket the top of the tower to entrain the various contaminants, is then passed through a scrubber to condense the hydrocarbons. The air is blown through the asphalt that is heated to 260°C, starting an exothermic reaction. Oxygen in the air reacts with hydrogen in the residuum to form water, and the reaction also couples smaller molecules of asphalt into large molecules to create a heavier product. The process is shown in Figure 18 (below).

During the process, coke will form on the oxidizer walls and the air sparger. The coke will need to be removed periodically, and can be processed along with off-spec coke from a refinery cooker, or disposed of to landfill.

Supercritical extraction

The Residuum Oil Supercritical Extraction (ROSE) process is based on the use of light, readily available paraffinic solvent (e.g. compressed liquid butane or pentane) to extract deasphalted...
oil from a feedstock rich in asphaltenes. The solvent is separated from the deasphalted oil in the downstream deasphalted oil separator, then recovered and recycled.

This is a closed process that produces waste sludge only from process upsets, turnaround and periodic inspections of the system. These wastes can be processed through the refinery slop oil system or sent to a coking unit.

**Asphalt emulsion**

Residuals from the vacuum distillation may also be upgraded to an asphalt emulsion by milling (or shear mixing) soap with the asphalt. These emulsions are used for road oils, where good adhesion is required.

This process generates waste streams from process upsets, turnaround and periodic inspections of the system.

**Good practices for minimizing residual upgrading waste**

- Process optimization to prevent upsets.

Where it would not cause negative effects, off-spec products from residual upgrading can, in some cases, be recycled back into the process. However, if contaminated or solidified, off-spec products will need to be disposed of (to landfill or by incineration). Note that the sludge can also be ignitable in addition to containing toxic constituents, and thus may require further characterization analysis.

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**Lube oil processing**

Vacuum column distillates are treated and refined to produce a variety of lubricants. The manufacture of lubricating oil base stocks consists of the following five basic steps:

- distillation;
- deasphalting to prepare the feedstocks;
- solvent or hydrogen refining to improve viscosity index and quality;
- solvent or catalytic dewaxing to remove wax and improve low temperature properties of paraffinic lubes; and
- clay or hydrogen finishing for improving colour, stability and quality of the lube base stock.

Most of the above processes, other than hydrogen refining, are the same as those covered above, and are not repeated in detail below.

**Lube distillation**

This process consists of atmospheric distillation followed by treatment in a vacuum distillation unit to separate the crude into various fractions. The majority of the lube stocks boil at a temperature between 305 and 535°C. Caustic solutions are sometimes introduced to the distillation feed to neutralize organic acids present in some crude oils, to reduce or eliminate corrosion in downstream processing units, and improve colour, stability and refining response of lube distillates.

**Lube deasphalting**

The most common process is propane deasphalting, used to remove asphaltenes and resins that contribute an undesirable dark colour to the lube base stocks. This process typically uses baffle towers or rotating disk contactors to mix the propane with the feed. Solvent recovery is accomplished with evaporators, and supercritical solvent recovery processes are also used in some deasphalting units.
Lube refining processes

Solvent refining/extraction and hydrogen refining processes are most typically used to remove aromatics and other undesirable constituents from lube oil base stocks, as well as improving the viscosity index and quality of lube base stocks.

The purpose of the solvent refining/extraction is to improve the viscosity index, oxidation resistance and colour of the lube oil base stock, and to separate the aromatic portion from the feedstock. The most commonly used solvents are n-methyl-2-pyrolidone (NMP), furfural and phenol. The products are refined oils for further processing, or finished lube base stocks. By-products are aromatic extracts, which can be used in the manufacture of rubber, carbon black and petrochemicals, or reprocessed in the refinery as FCC unit feed, or used for blending into fuel oil or asphalt.

Lube hydrogen refining uses catalytic treatment (nickel-molybdenum on alumina) of the oil with hydrogen to improve product quality. The purpose of this process is to saturate olefins, and improve colour, odour and the acid nature of the oil. Lube oil hydrocracking is also used to remove nitrogen, oxygen and sulphur, and convert the undesirable polynuclear aromatics and polynuclear naphthenes to mononuclear naphthenes, aromatics and isoparaffins that are typically desired in lube base stocks. Hydrocracking employs catalysts consisting of cobalt, nickel, molybdenum or tungsten on an alumina or silica-alumina-based carrier.

Lube oil finishing processes

Hydrogen finishing processes are mostly used in lube oil finishing processes. They are mild hydrogenation processes used to improve the colour, odour, thermal and oxidative stability, and demulsibility of lube base stocks. The lube oil is fed together with hydrogen over a fixed bed of catalyst (nickel-molybdenum) at moderate temperature and pressure to neutralize, desulphurize and denitrify lube base stocks. The treated oil is separated from unreacted hydrogen, which is recycled. The catalyst is easily regenerated with steam and air.

All of the lube oil processing operations described above generate sludge and catalyst wastes during turnaround and inspection of process units.

Good practices for minimizing lube oil processing waste

- Process optimization to extend periods between turnaround and inspection.

Wastes generated from lube oil processing are typically landfilled, due to their smaller volumes and reduced hazardous nature, but may also be managed by other methods such as incineration or used as fuels or for other reuse/recycle opportunities. The determination...
as to whether lube oil processing residues should be treated as hazardous should based on characterization studies.

H₂S removal and sulphur recovery

All crude oil contains some quantity of sulphur that should be removed at various points in the refining process to avoid deactivating catalysts, eliminate corrosives or to improve product quality. The predominant technique for sulphur removal in refineries is amine scrubbing of sour gas streams followed by recovery of elemental sulphur in a Claus unit with final sulphur removal in a tail gas treating unit. Caustic or water washes are often used in conjunction with, or instead of, amine scrubbing to remove sulphur, particularly in the liquid phase.

Amine scrubbing

Recirculating amine is used at a number of locations in a refinery, and then regenerated at one location. In an amine scrubber, gas and liquid hydrocarbon streams containing hydrogen sulphide and/or carbon dioxide are charged to a gas absorption tower or liquid contactor where the acid contaminants are absorbed into a counterflowing 'lean' amine solution (typically, monoethanolamine (MEA), diethanolamine (DEA) or methyldiethanolamine (MDEA)). The 'sweetened' gas or liquid is removed overhead, and the ‘rich’ amine is sent to a desorber for steam stripping, and then to a regenerator. In the regenerator, the acidic components are stripped by heat and reboiling action and are disposed of, and the amine is recycled. The amine absorption and regeneration process is illustrated in Figure 19.

The stripped gas is primarily H₂S, which is routed to the Claus process to convert it into elemental sulphur. A heat-stable salt sludge is produced in the regenerator that should be disposed of during turnaround and inspection. Amine containing heat stable salts is wasted from the regeneration system when it becomes off-spec and cannot be reused. Small amounts of lean amine can be treated in the refinery wastewater treatment plant if it is equipped with biological treatment, and amine is bled into the system very slowly. Otherwise it can be sent off-site for reclamation or disposal.

Figure 19 Amine sulphur removal process
Claus unit

The Claus process uses both thermal and catalytic-conversion reactions. It produces elemental sulphur by partially combusting H$_2$S with air at temperatures above 850°C to form a mixture of SO$_2$ and H$_2$S. The remaining H$_2$S is then reacted with the thermally produced SO$_2$ to form elemental sulphur in the thermal stage and the subsequent catalytic stages (containing activated alumina catalyst). The resulting sulphur from each step is condensed to its molten state and drained to a storage pit, while the gas is reheated and sent to the downstream catalyst reactor. The typical Claus unit, as shown in Figure 20, consists of the three stages to achieve an overall sulphur removal yield of 90–95%.

At the end of the third stage the remaining gas (or tail gas) is combusted and released to the atmosphere, or routed to a tail gas treatment unit to achieve greater sulphur reduction. Catalyst from the Claus units is periodically replaced during turnaround and inspection of the system, and sulphur is typically sold as a product, but can be disposed of as waste if no beneficial reuse options are available.

Figure 20 Claus process recovery process flow diagram

SCOT® tailgas unit

Tailgas units are used to increase the overall recovery of sulphur. The Shell Claus Off-gas Treating (SCOT®) process is the most common of these processes, and is shown in Figure 20. It consists of a hydrogenation reactor followed by amine scrubbing. In the hydrotreating reactor the tail gas is contacted with H$_2$ and converted to H$_2$S over a catalyst of cobalt/molybdenum on alumina. The reaction is exothermic and heat is removed from the gas in the reaction cooler. The gas is cooled further in a quench tower by a circulating water stream to a temperature that is suitable for amine treatment. A sour water stream is also produced from the quench tower. Amine scrubbing of the gas and regeneration of the amine is achieved by a process similar to that described above. The treated gas is sent to a simple thermal oxidizer to convert any remaining H$_2$S to SO$_2$ before discharge to the atmosphere. The stripped H$_2$S stream is returned to the feed of the Claus unit.

Sour water from a tailgas treatment unit is typically discharged to the refinery wastewater treatment unit. Spent catalyst is replaced during...
Good practices for waste minimization in H₂S removal and sulphur recovery processes

- Replacing cloth filters with etched metal mechanical filters to reduce change out and subsequent loss of amine to sewers.
- Installation of sumps to capture amine that is drained from the filters during change outs and recovery to the amine system.
- Process optimization to reduce catalyst changeouts in Claus units and tailgas treating units.
- Treatment of heat-stable salt sludge build-up through an ion exchange process to lengthen periods between amine replacements.

Wastes from sulphur removal and treatment should be treated or disposed of based on their hazardous characteristics. Typical hazardous materials present in wastes from sulphur removal plants are provided in the tables in the section on Sources of waste (pages 6–9). It should be noted that amine solutions are also corrosive and ignitable as well as containing toxic materials. Characterization studies on any particular waste should be performed to confirm an acceptable treatment or disposal method.

Adsorbent filtering

Filtering with a variety of materials is used to remove impurities via adsorption from many hydrocarbon streams. Much of the material used for adsorbent filtering is referred to as ‘clay’ when in fact it can be clay, salt, sand, activated carbon, molecular sieve or other materials. Typical applications of the different materials are summarized as follows:

- Clay applications are part of the isomerization, extraction, alkylaion, kerosene treatment and lube oil processes as described in the sections above.
- Activated carbon, coal or charcoal is used as the catalyst support for the Merox and Minalk systems that convert mercaptans in hydrocarbon streams to disulphides using oxygen and an organometallic catalyst in an alkaline environment.
Salt and sand are used for removal of water from products with low tolerances to water content (e.g. jet fuel). When hydrocarbon is passed through a fixed bed of sand, the moisture collects on the sand particles and eventually settles to the bottom of the vessel, where the water is removed. In a salt drier, water in the stream dissolves salt (e.g. sodium chloride) which then collects in the vessel bottom and is periodically removed. Salt and sand treaters are commonly found following aqueous treatments such as caustic washing, water washing, or Merex caustic treatment.

Molecular sieve is used for reactor feed preparations (e.g. precious metal catalysts are often deactivated by water) to selectively adsorb water and sulphur compounds from light hydrocarbon fractions such as propane and propylene. The hydrocarbon passes through a fixed bed of molecular sieve. After the bed is saturated, water is desorbed by passing heated fuel gas over the bed to release the adsorbed water and sulphur compounds into the regeneration gas stream, which is commonly sent to a flare stack. Molecular sieves are used in isomerization units, HF acid alkylation units, and in Dimersol® units.

Metal oxides are used to prolong platinum catalyst life by removing sulphur compounds before a catalytic reforming bed. The sulphur traps consist of granular or pelletized metal oxides, such as copper or magnesium. These materials adsorb entrained H2S, convert mercaptans to H2S and organic sulphides, and adsorb generated H2S. The material can then be desorbed, reactivated and reused.

Propane treating by alumina uses an activated alumina bed to de-fluorinate propane generated from a propane stripper. The propane is then dried in a sand tower and a drier, which also contains alumina. Alumina is also used to treat light naphtha prior to isomerization and to remove chlorides from hydrogen produced during the reforming process.

Entrained solids can be removed by in-line cartridge filters. These cartridges are commonly used for finishing kerosene, diesel and other fuels prior to sale.

Spent solid sorbents with liquid contents ranging from very low to oil-saturated material are generated in refinery filtering processes. The filter material is either inorganic (such as alumina, zeolite or clay) or organic (such as activated carbon). Depending on the process, filter media can remain in service for as little as a few months to as long as 10 years before the spent material is removed and the filter bed replaced.

The vast majority of adsorbent filter material is disposed of to landfill, although a significant amount may be recycled, and some of it is amenable to land treatment.

**Good practices for minimizing adsorbent filtering waste**

- Reuse spent alumina in cement plants.
- Transfer metal catalyst for reclamation and regeneration.

Waste adsorbent filter material should be treated or disposed of based on characterization studies to confirm an acceptable treatment or disposal method.

**Storage tanks**

Every refinery has on-site tanks for storage of refinery feed and products to maintain sufficient feedstock for continuous operations, for blending of crude and products, and to support product sales. Storage tanks are also used to store intermediate materials, and link continuous process operations with discontinuous operations. Storage tanks are sometimes used as process vessels in blending operations or as settling vessels. Waste materials are also sometimes stored in tanks prior to treatment on-site or transport off-site for disposal.
Regardless of a tank’s use, sediments from impurities in the stored material and corrosion material that forms in steel tanks (scale) accumulate over time and needs to be removed periodically, typically when the tanks are taken out of service for inspection and maintenance.

Sludge from many types of storage is hazardous, with characteristics that are similar to those of the material typically stored in them. Material from corrosion may also be hazardous.

**Good practices for minimizing storage tank waste**
- Use of in-situ treatment prior to removing the sediments from a tank (e.g. washing the tank with diesel, naphtha or water). The liquid carrying the organic fraction of the sediment is typically recycled to the crude unit via the recovered oil system;
- Use of separation techniques (a centrifuge or hydrocyclone) to pretreat tank bottom sludges prior to discharge of the liquids to wastewater treatment or the recovered oil system.
- Use of mixers to decrease sediment generation in crude tanks, except in cases where crude contains high amounts of entrained water. Apart from delivering homogenous feed to the crude unit, they also serve the function of entraining particulates and heavy hydrocarbon;
- Recycling of sediments in process units: the sediments of tank bottoms may be removed and used as feedstock in another on-site unit, such as a delayed coker, distillation unit, catalytic cracker or asphalt production unit. However, recycling of sediments can have serious negative effects (e.g. plugging of FCCU beds) so the use of this technique needs to be carefully assessed for risk at the facility.
- Use of sheeting near tank openings to collect spills during turnaround and inspection. Spill reduction decreases the quantity of contaminated soil to be disposed of with the tank sediment.

Waste from storage tanks is made up of sludge and metal scale from corrosion of the tank that has collected at the bottom. Sludge is made up of heavy hydrocarbons combined with organic and inorganic solids. It will have hazardous components similar to the material that was stored in the tank, which will only be determined through characterization studies.

Mechanical or hydraulic techniques should be employed to promote fluid agitation, ensure an adequate supply of proper additives and control temperature, in tanks that contain materials which are prone to phase separation, emulsification or deposition into the tank bottom, thus minimizing or preventing the generation of hazardous wastes.

Proper tank construction techniques, including the use of appropriate materials for their construction, and sampling procedures should be considered, to avoid losses of materials and the resulting generation of unnecessary solid wastes.

**Lead alkyl storage**

Tetraethyl lead and tetramethyl lead have been widely used historically as an octane boosting, anti-knock compound in gasoline, and continue to be used in the manufacture of aviation gasoline (avgas). As engine manufacturing has changed over time, and with the advent of other refining processes to boost octane, the use of these lead alkyl materials has been eliminated from new refineries and phased out in existing ones. However, where they still exist, and until the processes are completely decommissioned and removed from a refinery, they will generate waste.

Lead alkyls are flammable, corrosive materials that decompose over time generating dangerous by-products. Decommissioning and destruction of associated facilities should take place as soon as possible after they are no
longer required. Decommissioning of lead alkyl facilities requires special expertise, procedures and equipment to minimize environmental, health and safety risks. Waste material and sludge from the process should be handled and transported in special containers and should not be sent directly to landfill under any circumstances. Tanks and equipment used for storing and mixing lead alkyl compounds should be decontaminated prior to disposal of the scrap. Specific guidance for disposal of lead alkyl compound equipment and wastes is provided in the United Nations Environment Programme document entitled, *Recommended Practices for the Decommissioning Dismantling and Disposal of Lead Alkyl Compound Facilities and Equipment*.

**Coking unit**

Coking is a severe thermal cracking process used primarily to reduce refinery production of low-value waste fuel oils and some other hydrocarbon streams by transforming them into naphtha and diesel range products for blending into fuel products. The coking process produces petroleum coke, which is essentially solid carbon with varying amounts of impurities that can be sold as solid fuel.

A coker operates by heating the feed and then using a fractionator to separate off any naphtha and light hydrocarbons, which are recycled to other refinery processes. The bottoms from the fractionator are then heated again and fed into an insulated vessel at moderate pressures and high temperatures where they crack and lay down coke on the surface of the drum. Off-gas from the drum is recycled to the bottom of the fractionating column. When coke has lined the drum to a sufficient depth, it is taken offline while another drum is operated in parallel. The coke is then steamed to remove any remaining hydrocarbon vapour and then cut from the sides of the drum with high-pressure water lances. A process flow for a delayed coker is shown in Figure 22.

Cokers generate sour water and coke, which may be considered a product or a waste, depending on the availability of a market for the material and its quality.

**Good practices for minimizing coker waste**

- Minimize off-spec coke production through process optimization.
- Minimize coke spillage at loading facilities

**Hydrogen production**

Complex refineries require a continuous source of hydrogen for a number of process units, in particular hydrotreaters. Hydrogen is typically produced on-site in a refinery through the process of steam reforming, where a light hydrocarbon is partially combusted in an oxygen-poor environment to create carbon monoxide and some hydrogen. The mixture is then reacted over a nickel base catalyst to convert carbon monoxide and water to more hydrogen. This mixture is then cooled and
carbon dioxide is absorbed out of the gas in the solvent scrubber (using MEA or sulfinol), as shown in Figure 23. The solvent is then regenerated in a solvent stripper.

Waste catalyst is produced from hydrogen production periodically during turnaround and inspection.

**Good practices for minimizing hydrogen production waste**
- Pretreat fuel gas feed well to minimize catalyst deactivation.

**Utilities**

Boilers, furnaces, gas turbines and other heat producing plants are essential to refinery operations. They are typically fired with fuels produced on-site, including refinery fuel gas and heavy fuel oil, and often supplemented with natural gas brought into the refinery. They typically produce high-pressure and low-pressure steam that is routed throughout the refinery. Some direct-fired process heating also occurs.

Boiler blowdown is typically routed to the wastewater treatment plant. Wastes produced from boilers include non-oily sludge from blowdown treatment and boiler feedwater tanks. These are typically characterized, pretreated and disposed of to landfill as non-hazardous waste.
References


IPIECA is the global oil and gas industry association for environmental and social issues. It develops, shares and promotes good practices and knowledge to help the industry improve its environmental and social performance, and is the industry’s principal channel of communication with the United Nations.

Through its member-led working groups and executive leadership, IPIECA brings together the collective expertise of oil and gas companies and associations. Its unique position within the industry enables its members to respond effectively to key environmental and social issues.

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- African Refiners Association (ARA)
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