best available techniques to reduce emissions from refineries

Prepared for the CONCAWE Air and Water Quality Management Groups by its Special Task Forces AQ/STF-55 and WQ/STF-28

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ABSTRACT

BAT Reference documents (BREFs) are to be prepared by the European IPPC Bureau established at JRC/IPTS in Seville, and the Refinery BREF is scheduled for 1999. It is understood that the oil industry will be involved in the preparation of this document. The oil industry wishes to make a positive and informed contribution to the exercise, based on actual data on facilities installed in refineries, their capital and operating costs, and delivered performance capability. CONCAWE therefore established Special Task Forces WQ/STF-28 and AQ/STF-55 to study this subject. This report details their findings.

This CONCAWE report considers a wide range of emissions control techniques for refinery operations, the cost of installing and operating them, and the performance they have been demonstrated to deliver. The document is divided into five sections as follows:

I. General Introduction
II. Emissions to Air
III. Emissions to Water
IV. Waste
V. Soil and Groundwater

KEYWORDS

Air emissions, BAT, best available technology, BREF, cost, effluents, emissions, groundwater, IPPC, oil, pollution, refinery, sludges, soil contamination, treatment, wastes, waste water, water

NOTE
Considerable efforts have been made to assure the accuracy and reliability of the information contained in this publication. However, neither CONCAWE nor any company participating in CONCAWE can accept liability for any loss, damage or injury whatsoever resulting from the use of this information.

This report does not necessarily represent the views of any company participating in CONCAWE.

EXECUTIVE SUMMARY

This report has been prepared by CONCAWE to provide comprehensive information, based on actual user experience, for the development of Best Available Techniques Reference Documents (BREFs) for the oil refining industry. It is intended to serve as input to the refinery BREF development effort required under the Integrated Pollution Prevention & Control (IPPC) Directive. Also to provide a reference document for refineries when determining future investment needs. The oil industry wishes to make a positive and informed contribution to this exercise, based on actual data from installed facilities, their capital and operating costs, and their delivered performance capability. This report describes the techniques used to minimise and control air, water, and waste emissions/discharges, as well as those for the protection of soil and groundwater. Implications of pollution controls for energy use are also addressed.

Several important principles concerning BAT are reviewed in the report to ensure that the available techniques described are properly assessed in future considerations of their applicability as BAT, e.g.:

- There is no such thing as a "universal" BAT. Oil refineries differ in size, complexity, the types of processes they operate, and the crude oils they process. Climatic/environmental conditions and the location of the refinery (e.g. inland or coastal, etc.) influence the nature and disposal outlets of emissions and their impact on the environment. BAT therefore includes a site-specific content to account for these differences.
- It is the impact that emitted pollutants have on the environment into which they are discharged and not the simple availability of existing techniques/technology to control them to lower and lower limits, that should dictate the level of control required as BAT. This risk-based approach to BAT determinations will help ensure that society's limited resources are directed toward the most cost-effective controls that result in the largest possible environmental benefit.
- BAT costs are frequently quoted based on the hardware costs associated with their installation/implementation. This approach significantly under-estimates the actual cost of BAT application. The total costs, including those associated with the design, infrastructure preparation, and installation costs are often four times the hardware costs.
- The cost of "BAT" is significantly impacted by what level of control already exists at a refinery. For example, while application of a technology offering 99% emissions control may be cost effectively applied to an otherwise uncontrolled site, the same technology installed at a site which has previously invested in controls that are 97% effective would provide a very poor emission reduction return for the investment.
- Cross media impacts can often result from the application of controls. These should be considered in the risk assessment mentioned previously when assessing the wisdom of applying a BAT at a given location.
- BAT determinations should be used to help set appropriate emission levels for a given situation/location as a result of establishing the level that is required for environmental protection and that can be economically met. However, the affected facility should be allowed to demonstrate achievement of the specified level by the techniques of their choice.

The report is divided into 5 sections

I. An introduction covering considerations that apply to BAT for all media.
II. Air pollution.
III. Water pollution.
IV. Waste
V. Soil and Groundwater

The introduction elaborates on many of the points discussed concerning BAT above. The individual environmental media section contain technical descriptions of applicable BAT, and where available, tables of cost and performance data from actual European installations.

best available techniques to reduce emissions from refineries - introduction

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BAT Reference documents (BREFs) are to be prepared by the European IPPC Bureau established at JRC/IPTS in Seville, and the Refinery BREF is scheduled for 1999. It is understood that the oil industry will be involved in the preparation of this document. The oil industry wishes to make a positive and informed contribution to the exercise, based on actual data on facilities installed in refineries, their capital and operating costs, and delivered performance capability. CONCAWE therefore established Special Task Forces WQ/STF-28 and AQ/STF-55 to study this subject; this report details their findings.

This CONCAWE report considers a wide range of emissions control techniques for refinery operations, the cost of installing and operating them, and the performance they have been demonstrated to deliver. This particular section (I) considers general issues concerning the application of Best Available Technology (BAT) to refineries and topics common to emissions to all media.

KEYWORDS

Air emissions, BAT, best available technology, BREF, cost, effluents, emissions, groundwater, IPPC, oil, pollution, refinery, sludges, soil contamination, treatment, wastes, waste water, water

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I.1. INTRODUCTION

Over the past few years, European governments have progressively sought the application of Best Available Techniques (BAT) for environmental emissions control to a range of industrial sectors, including the oil industry.

The Integrated Pollution Prevention & Control (IPPC) Directive [1] has been adopted in the EU and this calls for a high level of environmental protection, based on BAT, taking into consideration economic viability and local factors. The Commission is working on the exchange of information on BAT between Member States and the preparation of EU-wide BAT Reference Documents (BREFs). These could assume great significance, since it is likely that legislators and control authorities will use them as a guide for establishing future emission limit values for selected emitting sources.

The BREFs are to be prepared for the European Commission (DGXI) by a European IPPC Bureau established in Seville, and the preparation of the Refinery Reference Document is scheduled for 1999. It is understood that industry will be involved in the preparation of these documents. The oil industry wishes to make a positive and informed contribution to the exercise, based on actual data on facilities installed in refineries, their capital and operating costs, and delivered performance capability. CONCAWE therefore established Special Task Forces WQ/STF-28 (Water Quality, Waste, Soil & Groundwater) and AQ/STF-55 (Air Quality) to study this subject.

This CONCAWE report considers a wide range of emissions control techniques for refinery operations, the cost of installing and operating them, and the performance they have been demonstrated to deliver. In other words, actual practical data and costs of installed equipment are presented, rather than the cost/performance claimed by the designers/vendors of the equipment. The information was gathered by means of questionnaires sent to all CONCAWE member companies' European refineries. The data are presented as a series of technical descriptions and tables of cost and performance.

The report consists of five main sections: an introductory section that describes the BAT concept and refinery types, pollutants and their sources, followed by sections on air, water, waste, soil and groundwater.

I.2. BAT FOR REFINERIES

I.2.1. THE CONCEPT OF BAT

Several methodological approaches can be used for decreasing refinery emissions, namely:

- To consider the refinery as one installation (a "bubble") and to identify the global emission limits not referring explicitly to any given technology or process.
- To make a breakdown of the refinery into various elementary functions which can be split up further into units that consist of different facilities. Examples of these are: functions such as distillation, treatment, utilities, storage and loading; units such as: FCCU (Fluidised Catalytic Cracking Unit), SRU (Sulphur Recovery Units), hydrotreating etc. and facilities which include furnaces, compressors, tanks, pumps, flares, vents, stacks, etc.
- To identify the Best Available Techniques for individual units and to decide on emission limits for each one.

All approaches have their advantages and disadvantages (see **Table I.1**).

Table I.1 Comparison of Three Methodological Approaches

Approach	Advantages	Disadvantages	References
Global (bubble)	Simple Easy to create a standard	No explicit technological analysis	Many directives in EU but for simpler processes
Function	Not too complex Rigorous Systematic	Not taking into account global emissions	Technical notes
Unit / Equipment	Systematic Rigorous	More complex Needs more frequent review for new processes appearing	Choice made in USA

The global (bubble) approach is more flexible than the unit approach and gives industry the choice on how to implement techniques to achieve emission limits in the most cost effective manner for each individual site. It is used in certain member States for establishing SO_2 and NO_x emission limits. In other member States the unit/function approach is used, which is the more prescriptive and often less cost effective for the same result.

The “BAT” concept can be described[*] as:

- **“Best”** for the protection of the environment and society as a whole.
- **“Available”** thus allowing implementation, under economically and technically viable conditions, taking into consideration the costs and benefits.
- **“Techniques”** can mean technology, design and construction, but also maintenance, operating procedures, commissioning and decommissioning procedures. It is thus a wide term, designed to include all factors relevant to the environmental performance of an installation.

The technical criteria for selecting a technique include:

- proven operation
- proven reliability
- availability
- long term viability, taking into account the existing plant and planned development
- availability of alternatives, (e.g., how does the technique compare with alternative options).
- cross-media impacts including material/energy usage, noise etc.
- economic viability

From the above criteria it is clear that a technique must be established in commercial operation before it can be considered and that it may be site specific. In addition, economic factors must be taken into consideration.

I.2.2. CONCAWE’S VIEW ON BAT

Industry's, and ultimately society’s, financial resources are finite, and need to be targeted to achieve optimum overall protection at viable cost. While it may be convenient to specify uniform controls throughout an industry, this may often not provide the greatest environmental benefit for the committed investment. The level of emission reduction should be based on the environmental quality objective(s) required, not just on the technical ability to achieve a specified level of control.

CONCAWE therefore proposes that the process to determine BAT consider:

- the **need** for controls based on the scientifically established environmental quality objectives and risk assessments, related to the use of the environmental compartments.

  For Example:
  - is the water used for: drinking, bathing, or fishing.
  - will the soil be used for: crops, housing, or industry
- the **degree** of control required based on environmental quality standards (i.e. sound science);
- the **type** of control required to meet these standards based on the cost of installing and operating it, and the required magnitude of the resulting reduction in discharges (i.e. cost/benefit).

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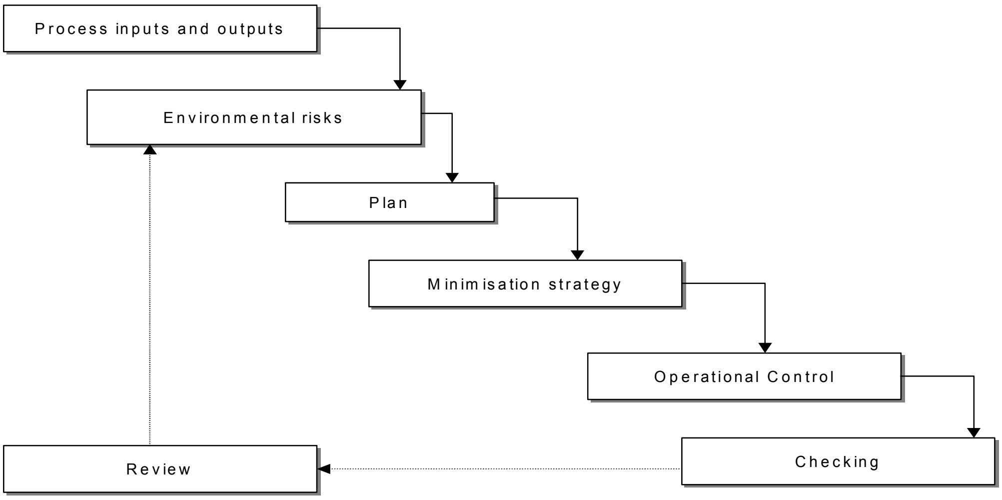
[*] Note that “BAT” is also defined in the IPPC Directive Article 2-11[1].

The Environmental Management Systems (EMS) cycle approach is suitable for IPPC (See also **Figure I.1**). The elements of EMS are listed below; these are worked out for waste management as an example.

- Assess the environmental risks of the installation as a whole.
- Plan all appropriate preventive measures against pollution and for continuous improvements (were significant risks exist).
- Apply the minimisation strategy:
  - Optimise the energy use, and/or recycle the potential wastes
  - Recover unavoidable wastes unless technically and economically infeasible
  - Dispose of wastes while avoiding or reducing negative environmental impacts using the best practical environmental option.
- Control operations to ensure the efficient use of energy, raw materials and implement measures to avoid and minimise incidents and their impacts
- Verify the performance of the process by direct or indirect monitoring
- Review the results

Figure I.1 IPPC Cycle



It is important to note the following considerations relating to BAT:

1. There is no such thing as a universal "BAT". Oil refineries differ in their size, complexity, the types of processes they operate, and the types of crude oil they process. They are also situated in a range of climatic and environmental conditions. All these factors influence the nature of their emissions, the impact these emissions have on the receiving environment, and the level of performance required from control techniques.

2. CONCAWE supports the move in Europe to first consider the effect that emissions have on the receiving environment: the risk based approach. In short this implies that not all emissions have to be zero in order to prevent a negative impact on the environment. These considerations fit more with the "global approach" as mentioned before.

3. In industrial areas the boundary for optimisation may be larger than the refinery; for example, heat integration between companies or between a company and a neighbouring town (district heating). Emphasising the use of air-cooling would, in this case, prevent initiatives of heat integration for many years. Another example would be a high calorific waste stream that can be used in a neighbouring industry as a fuel component.
4. Whenever a new technology comes on the market, legislators may want to see implementation of this new technique in a not too distant future. However, in case of add-on units, the remaining life of the existing unit needs to be taken into account.
5. It is important to consider the full implications of control measures employed. In particular, account must be taken of energy used for treatment, waste generation and environmental impact and cost of its disposal.

I.3. CROSS MEDIA ASPECTS

Technologies employed in the control and mitigation of one form of a pollutant will in many, if not most cases, either transfer the pollutant to another media, or require the consumption of energy to chemically transform it into a less hazardous form. In most cases, the determination of which form of an emission is most desirable and into which media the discharge would best occur with the least detrimental impact, will be very situation and site specific. It will be influenced by a multitude of locally defined circumstances, including: the availability and existing condition of air, water (both surface and subsurface), and land as emissions outlets. Furthermore the cost and availability of energy for the treatment of wastes, the regional waste handling infrastructure, and local regulatory preferences for certain control options. The existing operations and infrastructure of the industrial facility will also play a part in making this evaluation.

Some individual pollutant control technology tables contain a section entitled "other". Listed there are examples of the impacts on energy use and other environmental media resulting from the selection of the listed control technologies. In the water section of the report there is a discussion of the air emissions that occur during wastewater treatment and a section on the generation and methods of handling wastes resulting from wastewater treating operations. In fact, sludges produced during various wastewater treating processes are a very substantial fraction of wastes generated from refining operations, and these sludges are often incinerated (water to air impact) or landfilled/landfarmed (water to land impact).

The emphasis of the current effort is primarily on the identification of the best available technology to control emissions. However, it is important to recognise that many effective means of pollutant control, and efficient resource utilisation, are through implementation of processes and practices that minimise the generation of other contaminants requiring disposal, and/or the reuse/recycle of what are normally considered "waste" streams. These features are typically incorporated into a facility's base design. Conservation measures to reduce energy usage for utilities (electrical and steam) are a good example of this. Use of co-generated power and steam allows optimised use of energy resources. Use of other forms of waste heat within facility operations also reduces overall energy burdens. Reuse of materials such as the cascaded use of caustic soda so that it is used several times before being fully spent and disposed of as waste is another example of optimisation within a facility to reduce overall waste burdens. The use of one process effluent water in another process with lower water quality demands is a final example.

While it would be very helpful if some sort of general guidance could be provided to help guide decision makers in their selection between cross media impacts, local circumstances have such a dominant impact on this determination that it is virtually impossible to generalise such guidance. As mentioned before, what is important is that the industry and regulatory representatives use sound science and risk assessment criteria, associated with various disposal outlets, to identify the controls that make environmental, technical, and economic sense.

I.4. COSTS

I.4.1. INTRODUCTION TO COSTS

Since no new refineries are foreseen to be built in the medium term in Europe, the costs contained in this report largely reflect retrofitting rather than "grass-roots" installations. Retrofitting is inevitably more expensive than installation at the time of original construction, since it may be influenced to a significant extent by the need to clear plot space, to tie into existing facilities, and to build in areas that may already be congested with other operating equipment. The costs presented in this report are often higher than would be indicated by equipment vendor's data. It is important that costs used in assessing the cost/benefit of any future BAT decisions reflect actual installed costs and not equipment purchase prices. It must also be recognised that no two sites are the same, and the cost of installing particular facilities on one site may be very different from that for the same facilities on a different site - particularly if it is located in a different country.

Nevertheless assessments of the order of magnitude of capital and operating costs have been made based on European refinery data. In the tables that follow the cost is expressed in European currency (EUR 1999).

I.4.2. TOTAL ERECTED COSTS VS VENDOR EQUIPMENT COSTS

When trying to determine the cost of emission control technologies, it is often easiest to select a technology that appears to suit the requirements at hand, and solicit a cost quotation from a supplier of that technology/equipment. While fast and convenient, this approach can lead to vastly inaccurate estimates of the actual cost of the emission control technology. This occurs both on an absolute basis (cost/ton of emission reduced), and on a relative basis when comparing technology options. Different technologies can often have very different distributions of individual cost elements between the various types of costs that make up their total erected cost (e.g.: costs associated with hardware manpower, civil works, etc.).

Operating costs must also be critically considered when developing the absolute and relative cost comparisons of various control technologies. These can often be overlooked when taking a "hardware" view of control technologies, which is often the case when considering BAT. It is important to account for the potentially dramatically different operating costs between technology types depending on utilities usage, manpower requirements, waste generation potential and the cost of its disposal, etc.

Vendor costs will typically include only the cost of the specific equipment that the vendor supplies. In many cases this is a rather small fraction of the overall materials cost for a project. Additionally, the engineering costs associated with project design and supervision are often ignored, but can easily equal the cost of the vendor-supplied equipment. Expenditure often not thought of when estimating the cost of a project include items such as the need to: relocate existing facilities; enlarge and/or move existing sewer lines; perform soil investigations; develop new as-built drawings, process & instrumentation diagrams; modify existing piping and facilities such as blowers or pumps; etc..

In **Table AI-1**[a] you will find the cost distribution of the actual expenses incurred in the design and construction of a Vapour Recovery Unit (VRU) for a rail and barge facility. As indicated, the equipment traditionally viewed as comprising the VRU is all contained under the Direct Costs - Equipment category, and represents only about 20% of the total project cost. In this instance the indirect costs associated with engineering and overseeing the project were of exactly the same order of magnitude as the direct equipment costs. Together these did not even account for half of the total project costs. Over 50% of the cost of this project were spent for the non-equipment category which includes such things as piping, concrete and paving, instrumentation, electric power and light, etc.

In the **Table AI-2**: "Cost of reduction techniques", there is an example of an actual project; total erected cost.

I.4.3. RETROFITTING EXISTING INSTALLATIONS

Grass roots installations and existing operations/units require essentially the same technology/equipment to control specified pollutants, or meet specified emissions limits. The differences between them are essentially driven by the fact that in a grassroots case it is possible to ensure that all of the control technology requirements (i.e. plot space, utilities, structural support, etc.) are explicitly considered when the facility is designed. In the case of a retrofit, the original design choices may result in otherwise available or even preferred control technology(s) being of limited applicability or possibly even infeasible. Considerations of whether a technology constitutes BAT for a retrofit application deal primarily with the ability of the existing installation to meet the process, physical, and structural requirements of the control technology.

Depending on the nature of the control technology, its ability to be technically and economically retrofitted onto an existing facility can vary from being no more difficult than including it in a grassroots design, to being essentially impossible to utilise without rebuilding the entire existing process. This distinction in available technology's applicability to new and existing facilities is a crucial one to include in any determinations of what constitutes BAT. It forms the basis for the justifiable establishment of different BAT criteria for new and existing facilities and equipment.

The **Table AI-3** presents a qualitative view of the differences in the difficulty in installing a control technology in the grassroots vs. retrofit cases. The technology selected for comparison is combustion NO_x control. The upper portion of the table compares the significance of problems one might expect to encounter in installing these NO_x controls in grassroots and retrofit cases. Generally no problems should be expected in grass-root applications. In the case of the retrofit applications one can see that the difficulties encountered range from none in the case of steam injection, to incremental costs for furnace modifications in the Low NO_x burner case, to potential non-reconcilable incompatibility in the SNCR and SCR cases. The lower half of the table briefly presents some of the considerations that lead to these conclusions.

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[a] The tables preceded by a letter A in front are to be found in the Appendices.

I.4.4. CAPITAL AND EXPENSE CONSIDERATIONS

It is important to recognise the fact that different control techniques (both equipment-based controls and procedural techniques) can be very different in terms of the distribution of costs between capital and operating expenses. Some equipment costs while initially high are then very low in operating expense, while other very low cost equipment approaches involve severe increases in operating costs such as manpower, utilities, or expendable chemicals. It is generally easier to quantify the cost of hardware than the full implications of the likely expenses incurred by a technique. Also, equipment items will become more costly (in current EUR) over time due to inflation, etc. Decisions on the cost of BAT must explicitly and critically include both capital and expense factors in establishing the cost of controls. In certain tables in this report "other impacts" are identified associated with specific control techniques. We restricted these to cross-media and energy impacts, and did not include economic or other business implications. These however should not be lost in the evaluation of techniques as qualifying as BAT.

I.4.5. INITIAL EMISSION CONTROL VS INCREMENTAL CONTROL COSTS

An important consideration of the cost of BAT relates to the changing cost-effectiveness that results for a given technology depending on the point of control from which one starts the cost effectiveness calculation. Most BAT studies, including this one, present the cost and effectiveness (percent of emission reduction or tons of emissions reduced) of installing a technology or implementing a technique against an uncontrolled baseline operation. In this case it is easy to calculate the cost effectiveness of the proposed BAT versus an otherwise uncontrolled facility by simply dividing the cost of the BAT by the emissions reduction achieved. **Table AI-4** shows a series of various hypothetical controls capable of reaching various percentage emission reductions. For example, technology C would provide a 50% reduction for a cost of 2,000 k EUR (40 k EUR/% emission reduction) while technology G would provide 99% reduction for 12,000 k EUR (120 k EUR/% emission reduction).

Due to local regulations and/or corporate policies there are many situations where certain levels of control already exist within specific refineries. In these cases the cost for achieving a given % emission reduction target is significantly increased over the initial cost effectiveness values discussed for BAT in the previous paragraph. This needs to be accounted for in determining the cost effectiveness of a technology/technique qualifying for BAT. As can be seen in **Table AI-4**, if technology C is already in place at a location, the additional emissions reduction for going to technology G would be only 49%. The cost of implementing technology G therefore becomes ~240 k EUR/% for the incremental emissions reductions, rather than the 120 k EUR/% when going to 99% control from 0%. If one were to go to technology G in a location where technology E was in place, the incremental cost would be 1,200 k EUR/% reduction. In all of these instances the final situation is to be at 99% control of emissions. The actual cost for going to the 99% level in these situations, if done incrementally, would effectively be the cost of implementing Technology C plus E, plus G, to get the 99% reduction. **Table AI-5** shows the resultant cost of applying various technologies starting from different levels of existing control. This is also shown graphically in **Figure AI-1**.

It is considerations such as those described in the preceding paragraphs that require BAT to be determined on a site-specific basis, taking into account the existing control situation in existence to meet the specified environmental quality objectives.

I.5. BRIEF DESCRIPTION OF A REFINERY

I.5.1. REFINERY PRODUCTS AND PROCESSES

The essential function of oil refineries is to produce marketable hydrocarbon-based products and intermediates, from crude oil or other hydrocarbon feedstocks.

A refinery produces a wide variety of products of different specifications:

Fuels

- Liquefied Petroleum Gases (LPG)
- Gasolines of different grades (e.g.: automotive and aviation gasolines)
- Kerosenes (e.g.: aviation turbine and illuminating kerosenes)
- Gasoil/diesel-oil (e.g.: automotive and marine diesel)
- Light fuel-oils (e.g.: distillate heating fuel)
- Heavy fuel-oils
- Marine bunker fuel

Petro-Chemical feedstock

- Naphtha, gasoil, ethylene, propylene, butadiene, benzene, toluene, xylene

Other products

- White oils
- Lubricating oils, greases and waxes
- Bitumen
- Petroleum coke
- Sulphur

In order to produce end products from its feedstocks, a refinery carries out a number of processes. These processes are carried out in a number of installations, or plants, each of which has its own specific function, the output of one installation forming the input of other installations, as well as end products. These installations are supported by a number of other plants which supply utilities for the entire refinery - steam, power, water, hydrogen, etc. Since most of these refinery processes require a lot of energy, most have programmes for heat integration and energy saving.

The major categories of refinery installations are listed below:

Physical separation processes

- Atmospheric distillation
- Vacuum distillation
- High pressure distillation
- Aromatics extraction
- De-waxing/de-asphalting
- Gas separation plant

Processes which bring about chemical conversions

- Isomerisation
- Alkylation
- Etherification
- Reforming
- Catalytic cracking
- Hydrocracking
- Thermal cracking/visbreaking
- Petroleum coking
- Asphalt blowing

Purification or treating processes

- Desalting
- Hydrotreating/hydrodesulphurisation (HDS)/hydrofinishing
- Sour gas concentration (Acid gas removal)
- Sulphur recovery from hydrogen sulphide
- Sour water treatment

Lubricating oil refining

Utilities and General facilities

- Steam and/or power supply
- Refinery liquid/gas fuel system
- Flare system for disposal of vapour releases
- Water, Air, Hydrogen, Nitrogen supply
- Cooling water system
- Wastewater and hydrocarbon slops treatment

Blending, storage and loading facilities

Environmental Controls

- Aqueous effluent treatment
- Combustion and other air emission controls
- Waste disposal
- Odour and noise control

Also covered are furnaces and boilers, which are operated as an inherent part of, and primarily for the purpose of, a process described above. Guidance is given for flares; incinerators, large boilers and furnaces with a net rated thermal input of 50 megawatts or more, including aggregate plants (such as combined cycle).

I.5.2. REFINERY TYPES

Refineries vary greatly in their complexity, that is, in the number of different types of operations carried out. The simplest type uses mainly physical separation processes such as distillation with only limited use of conversion processes such as mild hydrotreating and reforming. These so-called "hydroskimming" refineries carry out very little conversion of products. This means that the types and quantities of products are largely determined by the composition of the crude oils processed. It cannot be influenced to any great extent by modifying the operating mode of the refinery.

In a hydroskimming refinery, crude oil is refined by fractionation into straight run naphtha, kerosene, gasoil and atmospheric residue in the atmospheric distillation unit. The naphtha, kerosene and gasoil fractions may be treated in hydrodesulphurisation (HDS) units. The hydrotreated naphtha is split into a light and a heavy naphtha stream. The heavy fraction is upgraded in the catalytic reformer to produce a high-octane gasoline blending component. Blending of the components from these operations produces the final products.

Gas streams from the HDS units and catalytic reformer are passed to the gas plant where they are separated into a C_3 stream and a C_4 stream. The lighter gases (C_1 and C_2) are sent to the refinery gas system for burning in the refinery's own boilers and furnaces. "Sour" gases, i.e. those containing sulphur compounds, are treated in a sour gas removal unit (amine treating), and H_2S rich gas is passed to the Sulphur Recovery Unit, where most of the H_2S is converted into elemental sulphur. The waste gas is incinerated or passed to a "tail-gas" unit for further treatment.

The distribution of products produced in a hydroskimming refinery will depend on the nature of the crude(s) processed. Lighter crudes will produce a higher proportion of lighter products such as gasoline and gasoil, whereas heavier crudes will produce heavier fuel oil. The product profile from a hydroskimming refinery particularly in respect of heavier crudes does not correspond well with the average demand profile in European countries. The production of gasoline and middle distillates, for which there is greatest demand, will generally be insufficient.

Increasingly complex refineries make more extensive use of conversion processes such as severe hydrotreating and catalytic cracking in order to shift their product spectrum towards the higher value and lighter liquid products.

Installation of conversion units such as cat-cracking, hydrocracking, coking etc. are the means by which refineries both obtain a better match between production and demand, and increase their flexibility. This flexibility is attained by variation of the fraction of atmospheric residue or other feedstock subjected to conversion, and by the "severity" of the conversion process, determined by variation in the operating conditions. By increasing the conversion capacity (severity), the energy required will also increase, consequently the emissions to atmosphere.

Among refineries, which carry out some conversion, can be the following types:

- **mild conversion** refinery with a limited conversion capacity (visbreaker or thermal cracking unit)
- **complex refinery** with the addition of a fluid catalytic cracker and/or a hydrocracker and/or a coker.

In all these refineries, solvents, lubricants and/or bitumen may be produced.

In the appendix **Figures AI-2**, **3 and 4,** typical flow schemes for the three refinery types described have been given. These are simplified schemes and do not show all the purification or treating facilities and specialities such as storage, utilities and lubricating oil manufacturing.

The complexity of refineries has increased in the European Union, with the installation of additional conversion units (e.g. thermal-, catalytic- and hydro-crackers) as the demand for fuel oil production decreases and the demand for a higher yield of gasoline and other light products increases. This is shown in **Figure AI-5.** The added conversion capacity requires increased use of fuel, resulting in additional emissions of combustion products. Also, with more units, piping and storage tanks, fugitive emissions due to leaks and evaporation are increased.

I.5.3. EMERGING REFINING TECHNOLOGIES

There is a dilemma between the need for cleaner fuels and emission reduction already in use in European refineries. The additional and more severe processes to deliver cleaner products by itself increase the (mainly CO_2) emissions from refineries. For example deep conversion units transform heavy hydrocarbons from the vacuum residue into lighter products.

Two main processes of deep conversion are:

- thermal processes with or without catalyst
- hydrogen addition processes.

These processes are already in use in European refineries, and are available through several licensors.

Separate from the lighter products, these processes may produce:

- high heating value gas
- low sulphur fuel oil
- low heating value gas in case of the Flexicoking process

All these are used as refinery fuels.

Nevertheless, the application of these processes is expensive and often requires important changes in the refinery apart from the installation of the conversion unit itself (new hydrogen production capacity, retrofitting of vacuum distillation, changes in the fluid catalytic cracking unit, etc). The total cost of the implementation of a deep conversion unit in an existing refinery is reported to be in the range of 500 to 1000 million EUR.

The decision to make such an investment in a refinery depends on two conditions:

- the need to produce more light products than previously due to the changing demand structure
- requirement for producing products (especially fuel oils) with low sulphur content, due to regulations on sulphur content of oil products (e.g. the EU Auto Oil Programme to provide cleaner products)

It is generally a combination of these reasons, and the overall project economic viability, which contribute to the decision to make the investment.

It should be noted that deep conversion increases the energy consumption of the refinery and creates higher CO_2 emissions. Discussions in Europe about a further improvement of product quality will have a significant impact on the refinery technologies used. For example, a decrease of the aromatic content or an increase in cetane number of diesel will require new investments in hydrogenation capacity.

I.6. MONITORING OF EMISSIONS

Refinery operators obviously have a need to monitor their process performance. Environmental legislation has led to the need to monitor for compliance. If these needs can be combined the most cost effective monitoring solution is found.
The key point for all parties concerned should be that reliable information is generated. The required reliability, accuracy and frequency of monitoring should be related to the significance of the emission/potential environmental impact of a release i.e.:

- Environmental risk of the emission
- Level of the emission
- Properties and environmental fate of the compounds

It is desirable that Industry and Members States use similar measurement and reporting standards.

Emission monitoring can be done via direct and via indirect monitoring. In direct monitoring the emissions are directly measured i.e. if an SO_2 analyser is applied in a stack this is called direct monitoring.

Indirect monitoring can be done by calculation in combination with measurement of emission relevant parameters. For example: SO_2 emission can be established by the analysis of the sulphur content of the feed and the measurement of the flue gas flow. In systems subject to fouling, indirect monitoring is always the most reliable way of monitoring.

Emission relevant parameters for indirect monitoring can be:
- Temperature (e.g. thermal oxidisers)
- Pressure drop (e.g. venturi scrubber)
- Plant efficiencies
- Electric current (e.g. Electrostatic precipitator)

For both technical and practical reasons, it is normally not feasible to conduct direct measurements of emissions from diffuse sources. The way to avoid disproportionate emissions from such sources is a concerted programme of preventive maintenance combined with close plant surveillance by the plant operators.

Measurements can be done intermittently or continuously. Continuous monitoring is not necessarily more reliable or more accurate than other means, i.e. the indirect and direct monitoring. Critical factors and conditions for pertinent use of continuous monitoring are:

- Availability of equipment
- Accuracy and reliability of equipment (avoid false alarms)
- Ability and time to react of people being trained to take appropriate decision
- Ability to influence the process by implementing corrective actions
- Need for regular maintenance/calibration and confirmation of the result by laboratory analysis, e.g. in case of an incident

It is also important to recognise that so-called “self-monitoring” at own cost, can be required by the authorities. In this case industry should be free to select the most cost-effective solution. Nearly always this would be indirect (process parameter) measurement rather than direct (e.g. air quality) monitoring.

Emissions monitoring equipment should have provisions for zero and calibration checks and provisions for alternative testing in the event of breakdown or suspected malfunction. The regular observation of monitoring equipment by plant operators for detecting abnormalities in the process operation is as important an aspect of monitoring as is the compliance function, and forms part of a quality or environmental management system.

I.7. REFERENCES

1. EU (1996) Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. Official Journal of the European Communities No. L257, 10.10.1996
2. CONCAWE (1998) Trends in oil discharged with aqueous effluents from oil refineries in Europe - 1997 survey. Report No. 8/98. Brussels: CONCAWE

APPENDIX I

Table AI-1 Example of Actual Project; Total Erected Cost

Vapour Recovery Unit (VRU) - Barges & Railcars (1997)

DESCRIPTION		**k EUR**	**%**
INDIRECT COSTS			
230	Detailed Engineering	275	7
213	Field Supervision	137	3
213	Inspection	83	2
260	PMT - NPQC - Owner	424	10
	Subtotal	919	22
DIRECT COSTS - EQUIPMENT			
311	Heat Exchangers	0	0
314	Towers	0	0
315	Drums	0	0
316	Reactors	943	22
324	Pumps and Drivers	13	<1
326	Tanks and Spheres	0	0
347	Cooling Towers	0	0
	Subtotal	956	22
DIRECT COSTS - NON EQUIPMENT			
208	Scaffolding	25	<1
209	Cleanup Construction	8	<1
216	Construction Equipment	16	<1
307	Excavation & Cable Trenches	142	3
308	Concrete Work and Paving	216	5
309	Piling	33	1
313	Piping	1179	28
318	Structural Steel	77	2
322	Instrumentation	285	7
328	Roads, Walks, Fences	15	<1
337	Electric Power and Light	107	3
345	Communication Equipment	0	0
348	Insulation	3	<1
349	Paint	167	4
380	Standby Equipment (Cap. Spare)	0	0
	Subtotal	2273	54
	Total Capital	4,148	98
EXPENSE			
101	Dismantling	17	<1
102	Site Clearance	0	0
103	Relocation	7	<1
104	Reconditioning	0	0
105	Temporary Bypasses	0	0
111	Gas Freeing & Cleaning	8	41
165	Owner Expense Charges	81	2
	Subtotal	113	2
	Final Total	**4,261**	**100**

Table AI-2 Example of Actual Project; Total Erected Cost

Tail Gas Cleanup Unit (3rd Stage Claus plus Super-Claus (1997))

DESCRIPTION	**k EUR**	**%**
INDIRECT COSTS		
Detailed Engineering	8.0	27
Field Supervision	1.6	5
Owner	2.4	8
Subtotal	12.0	40
DIRECT COSTS – EQUIPMENT		
Materials	7.3	25
Catalysts and Chemicals	0.6	2
Subtotal	7.9	27
DIRECT COSTS - NON EQUIPMENT		
Subcontracts	8.6	29
Temporary Construction & Consumables	0.4	1
Subtotal	9.0	30
Total Capital	28.9	97
EXPENSE		
Licensing Fee	0.5	2
Subtotal	0.5	2
Final Total	**29.4**	**99**

Table AI-3 Retrofit (NO_x) Problems Relative to Grassroots Installations

	Low NO_x Burners	SNCR	SCR	Steam Injection
Retrofit Application	Higher Cost	May not be applicable	May not be applicable	none

Some of the technical considerations behind the above table are:

	Low NO_x Burners	SNCR	SCR	Steam Injection
Equipment requirements	Individual burners	NH_3 injection system, NH_3 supply system,	NH_3 injection system, NH_3 supply system, catalyst	Injection nozzles, source of steam
Process requirements	None	Appropriate temperature window	Appropriate temperature window	None
Physical requirement	Adequate space below furnace floor.	None	Adequate plot space for catalyst bed	None
Structural support requirement	Furnace floor modification	No	Substantial catalyst support structure	No
Drop-in capability	Most likely yes	No	No	Yes

Table AI-4 Control Cost vs Emission Reduction

Technology	Percent Reduction	Technology Cost (k EUR)
A	0	0
B	20	1 000
C	50	2 000
D	60	3 000
E	90	4 500
F	95	7 000
G	99	12 000

Table AI-5 Initial Control Cost vs Incremental Control Cost

Level of Control (%)	Cost to Achieve Control (k EUR)	Cost/% reduction from 0% starting point (k EUR/%)	Cost /% reduction from 50% reduction baseline (k EUR/%)	Cost/% reduction from 90% reduction baseline (k EUR/%)
0	0	NA	NA	NA
50	2,000	40	NA	NA
90	4,500	50	~110	NA
99	12,000	~120	~240	~1 200

Figure AI-1 Technology Cost Comparison

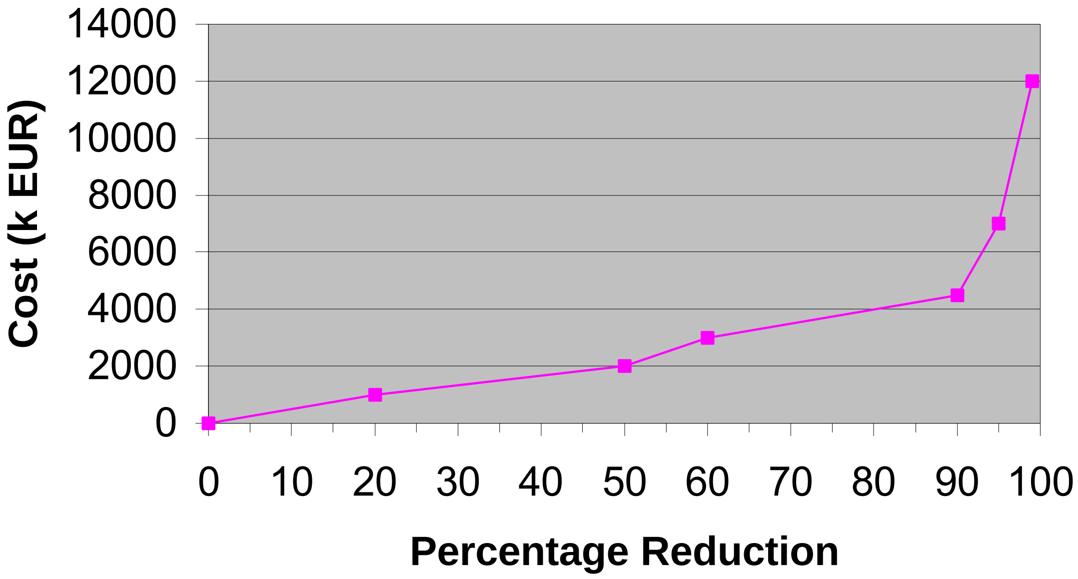
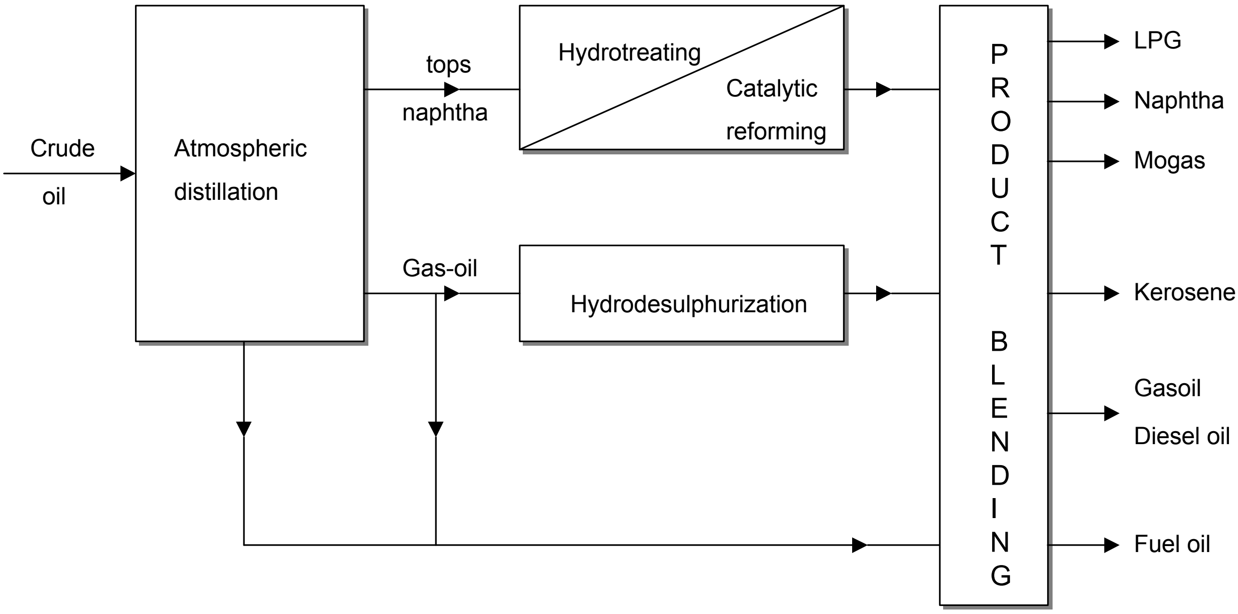


Figure AI-2 Typical Flow Scheme Hydro-skimming Refinery



Figures AI-1, 2 and 3 are typical flow schemes for the three refinery types described. These are simplified schemes and do not show all the purification or treating facilities and specialities such as storage, utilities and lubricating oil manufacturing.

Figure AI-3 Typical Flow Scheme Mild Conversion or Semi-complex Refinery

Thermal cracking is added.

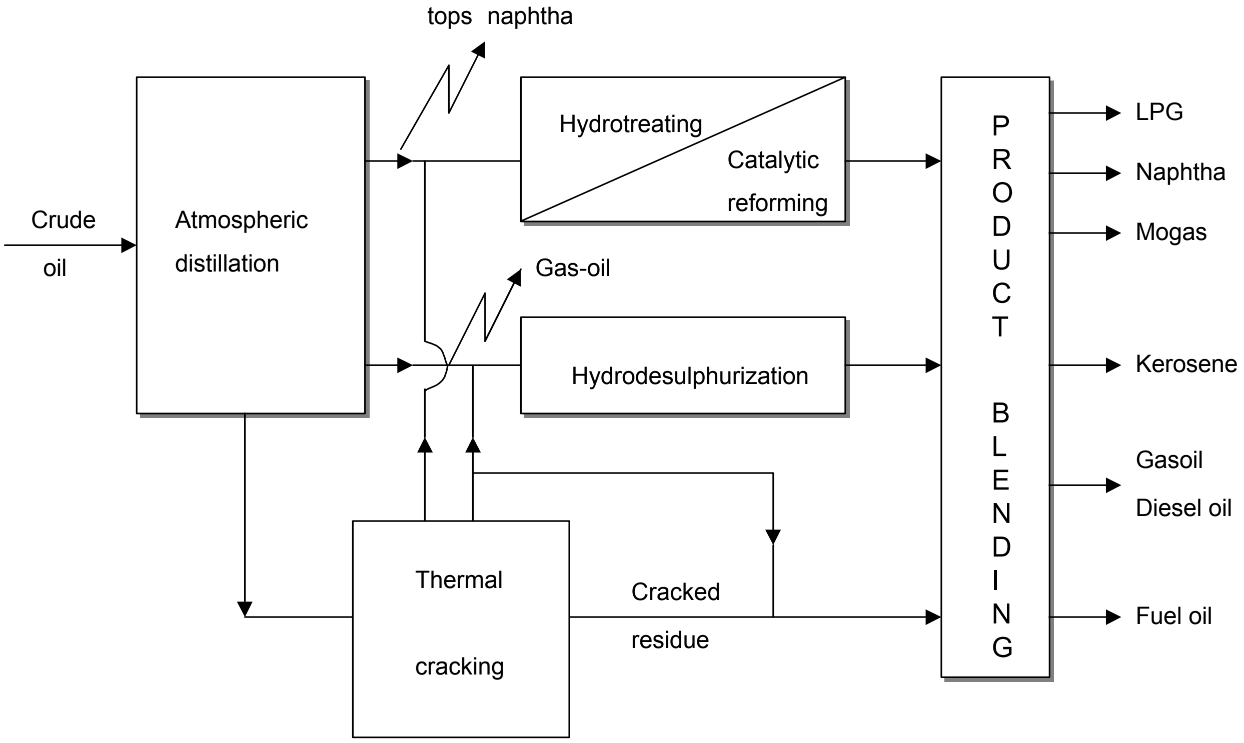


Figure AI-4 Typical Flow Scheme Complex Refinery

High vacuum distillation and cat cracking have been added

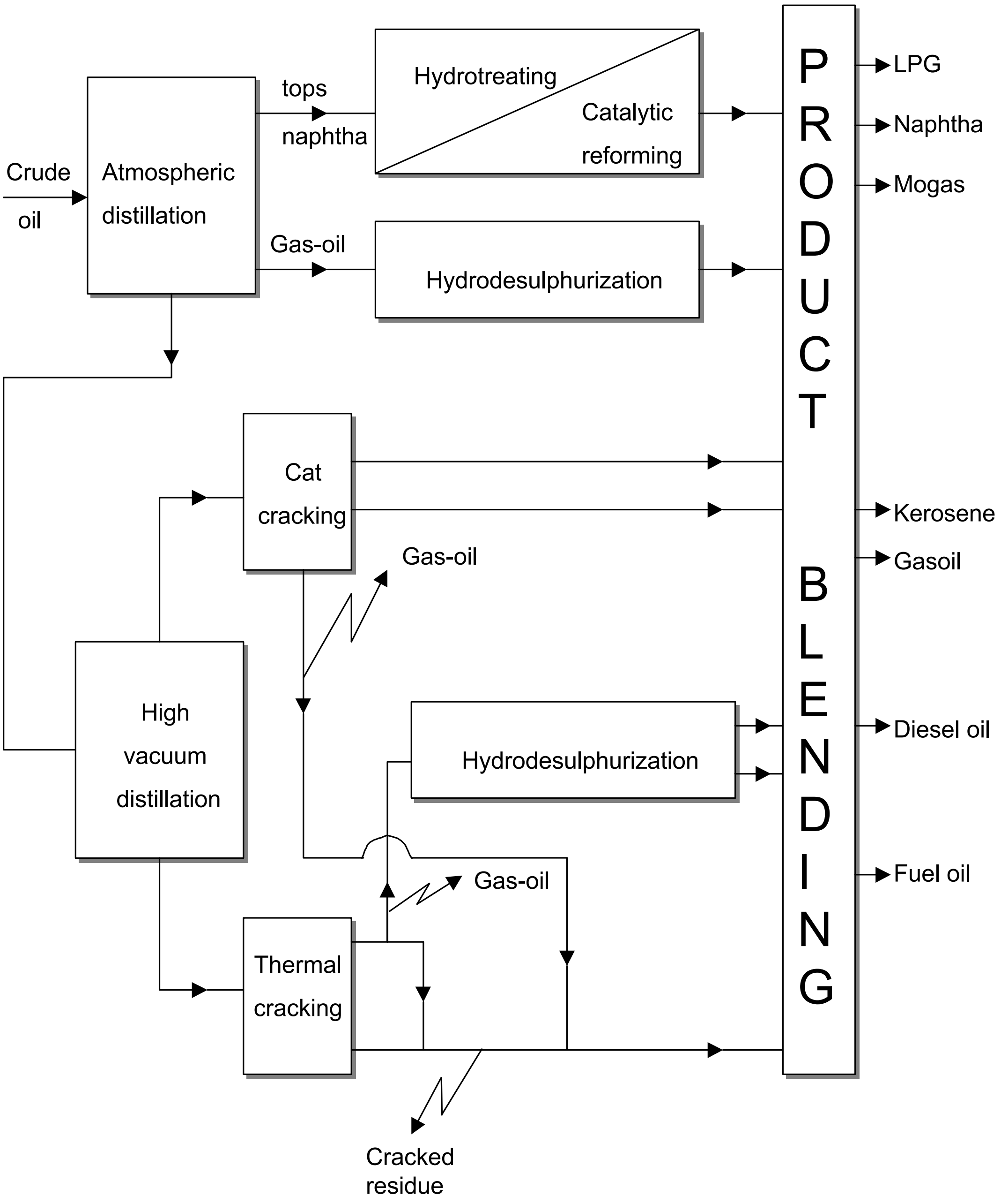
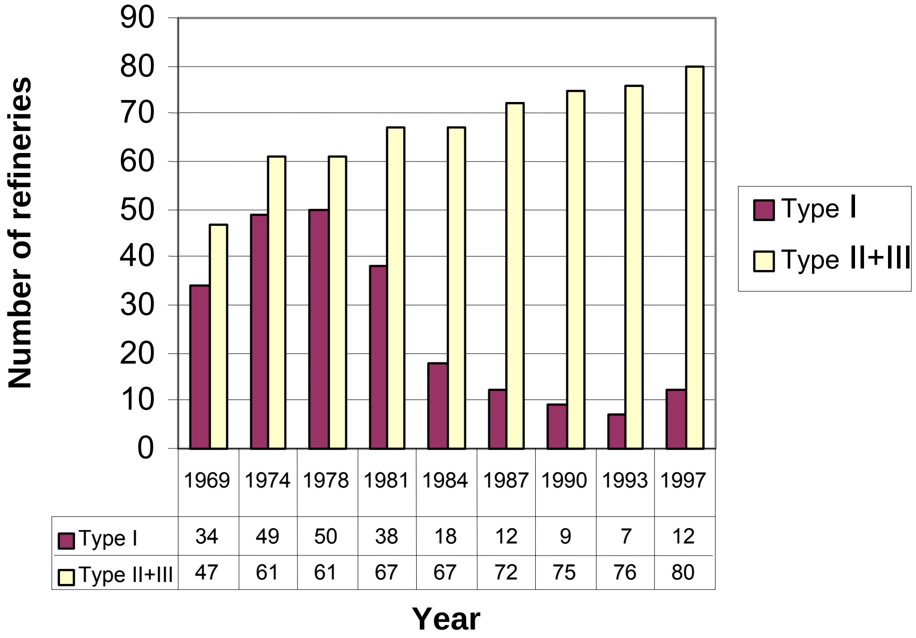


Fig AI-5 Increased Complexity of European Refineries



	1969	1974	1978	1981	1984	1987	1990	1993	1997
■ Type I	34	49	50	38	18	12	9	7	12
□ Type II+III	47	61	61	67	67	72	75	76	80

Notes:

Type I: Simple (non-conversion refinery: composed of crude oil distillation, reforming, treatment of distillate products, including desulphurisation and/or other quality improvement processes (i.e. isomerisation or speciality manufacturing)).

Type II: Mild conversion (Type I plus thermal cracking or visbreaking).

Type III: Complex (Type II plus fluidised cat cracking and/or hydrocracking).

Note: Any of above types may have bitumen or luboil production, this clearly increases the relative complexity

As can be seen from **Figure AI-5**, the number of simple type **I** refineries has decreased over the years. To make more efficient use of the crude, increasingly deeper conversion units have been installed in European refineries, resulting in higher energy consumption and thus an increase of emissions. Data derived from CONCAWE report no. 8/98[2] (**Table 2**).

best available techniques to reduce emissions from refineries – air

Prepared for the CONCAWE Air Quality Management Group by its Special Task Force AQ/STF-55

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ABSTRACT

BAT Reference documents (BREFs) are to be prepared by the European IPPC Bureau established at JRC/IPTS in Seville, and the Refinery BREF is scheduled for 1999. It is understood that the oil industry will be involved in the preparation of this document. The oil industry wishes to make a positive and informed contribution to the exercise, based on actual data on facilities installed in refineries, their capital and operating costs, and delivered performance capability. CONCAWE therefore established Special Task Force AQ/STF-55 to study the subject of air emissions from refineries and this report details the findings of the latter.

This CONCAWE report considers a wide range of emissions control techniques for refinery operations, the cost of installing and operating them, and the performance they have been demonstrated to deliver.

KEYWORDS

Air emissions, BAT, best available technology, BREF, cost, emissions, IPPC, oil, pollution, refinery, treatment

NOTE
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This report does not necessarily represent the views of any company participating in CONCAWE.

CONTENTS

II.1. OVERVIEW OF AIR EMISSIONS

In an oil refinery marketable products are made from crude oil. For most refineries the number of products is limited and fairly well defined, although the volumes may be large. There are some refineries that make speciality products such as lubricants and solvents. On a macro scale the crude oils vary only to a certain extent in their composition. Consequently the types of emissions to the environment from refineries is well defined.

The refinery processes can be broadly categorised as:

- heating hydrocarbons for processing
- physical separation and purification
- chemical conversion, such as residue upgrading
- cooling of the products
- storage of crude oil and products.

Refinery processes require a lot of energy; typically more than 60% of CO_2, SO_x, and NO_x emissions are related to the raising of energy for the different processes.

This section concentrates on emissions to air, their abatement techniques and the related costs. Other environmental issues from refineries such as the management of wastewater, of waste and soil and groundwater, are dealt with in other sections of the report.

An overview of the atmospheric emissions, their sources and main abatement techniques are given in **Table II.1**.

Table II.1 Overview of Air Quality Issues in Refineries

EMISSION	**AIR QUALITY RELATED ISSUES**	**EMISSION SOURCE**	**CONTROLS / BAT**
CO_2	Post-Kyoto Protocol UN/Greenhouse gas convention (93/76/EEC, 93/389/EEC)	Process furnaces/ Boilers, Gas turbines FCC regenerators Flare system Incinerators	Energy efficiency: heat integration/recovery, Use fuels with high hydrogen contents Monitoring/ evaluation/ strategies
SO_x	EU/UN-ECE, Acidification Strategy EC Directives: LCPD, SLFD, IPPC, Air Quality Directives: Sulphur protocol (incl. Bunkers), AQFD, National Ceilings Directives Other: UN-ECE/-WHO, OSPARCOM, US-EPA/ 1990 Clean Air Act	Process furnaces/ Boilers, Gas turbines SRUs FCC regenerators Flare system Incinerators Decoking operations	SRU: 3rd reactor, new design, Tailgas clean up unit. FCC: De-SO_x catalyst, Feedstock desulphurisation, Flue gas desulphurisation, Wet-scrubber. Refinery fuel system, Low sulphur crudes, Gas firing
NO_x	EU/UN-ECE , Acidification Strategy EC Directives: LCPD, IPPC, Air Quality Directives: AQFD, N-protocol (93/361/EEC) National Ceilings Directives Other : UN-ECE/-WHO, OSPARCOM, US-EPA/ 1990 Clean Air Act	Treating units Process furnaces/ Boilers, Gas turbines FCC regenerators Incinerators, Gas turbine, Flare system	FCC: CO/NO_x optimisation, Selective (non) catalytic reduction, Thermal de-NO_x, Low NO_x burners, Steam/water injection
VOC	EU/UN-ECE, Air Quality Directives AQFD, (94/63/EC), UN-ECE/VOC Protocol Stage I (Marine VR), Stage II MARPOL Convention Annex VI; IMO-MARPOL 73/78 National Ceilings Directives, Ozone Strategy Other: UN-WHO, US-EPA/1990 Clean Air Act, Draft EC-Long range transboundary air pollution	Storage & handling, Loading (incl. barges) Oil/water separation systems Fugitive emissions (leaks) Vents, Flare Air blowing, blowdown systems	Stage 1A: Vapour recovery system, Floating roof, Internal-floating cover. Stage 1B Vapour return. Other: Incineration, Leak detection and repair, Pressure/Vacuum valves, dry oil collection systems, automatic drains.

1. LCPD = Large Combustion Plant Directive
2. AQFD = Air Quality Framework Directive
3. SLFD = Sulphur in Liquid Fuels Directive
4. IPPC = Integrated Pollution Prevention Control Directive
5. BAT = Best Available Technique
6. WHO = World Health Organisation
7. OSPARCOM = Oslo/Paris Conventions for prevention of Marine Pollution
8. IMO = International Maritime Organisation
9. IPCC = International Panel on Climate Change
10. PAH = Polynuclear Aromatic Hydrocarbons
11. UN = United Nations
12. UN-ECE = United Nations - Economic Commission for Europe

Table II.1 *continued*

EMISSION	AIR QUALITY RELATED ISSUES	EMISSION SOURCE	CONTROLS / BAT
PM	EU/UN-ECE, EC Directives: IPCC, LCPD, Air Quality Directives: AQFD, Other: UN-WHO, US EPA	Process furnaces/ Boilers, FCC regenerators Coke plants Incinerators, Decoking, Flare	FCC: 3rd cyclone, Multi cyclones, Electrostatic precipitator, Wet scrubber
CO	IPPC UN/Greenhouse gas convention Other: UN-WHO	Process furnaces/ Boilers, Gas turbines FCC regenerators Flare system Incinerators Cold vents	Regulate Combustion process Monitoring/ evaluation: Inventory/Measurement Methods/Strategies Reduction
CH_4	Post-Kyoto Protocol UN/Greenhouse gas convention (93/389/EEC)	Storage & handling (loading) Cold vents Leaks	Flaring rather than cold vent, True Vapour Pressure (TVP) control, Maintenance, Monitoring/ evaluation: Inventory/Measurement, Methods/Strategies, Reduction
HALON	UN Montreal Protocol (94/84/EC)	Firefighting Equipment	Technical change fire-fighting systems. Stock management - phase out
CFC	UN Montreal Protocol (94/68/EC)	Refrigeration Airco systems	Technical change refrigeration/airco systems - phase out
Ni	Air Quality Directives, AQFD IPPC, UN-ECE protocols on Heavy Metal, OSPARCOM	See PM and SO_2	See PM and SO_2
Benzene	Air Quality Directives, AQFD, IPPC	See VOC	See VOC
PAH	Air Quality Directives, AQFD, IPPC, UN-ECE POP protocol, OSPARCOM	See VOC	See VOC

1. LCPD = Large Combustion Plant Directive
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10. PAH = Polynuclear Aromatic Hydrocarbons
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II.1.1. MAIN AIR POLLUTANTS

Annex III of IPPC Directive 96/61/EC[1] contains an indicative list of the main polluting substances to be taken into account for fixing emission limit values, among which the following are relevant for the refineries:

- Sulphur dioxide (SO_2) and other sulphur compounds,
- Oxides of nitrogen (NO_x) and other nitrogen compounds,
- Carbon monoxide (CO),
- Volatile Organic Compounds (VOC), in particular hydrocarbons (excluding methane),
- Particulate Matter (PM), including metals and their compounds
- Substances proved to possess carcinogenic properties.

Although not specifically mentioned, CO_2 emissions are considered to be a major issue by governments. Energy optimisation efforts that are standard practice in all refineries, are also the main means of control for CO_2. Some more specific controls are also discussed in this report

CO emissions are mainly associated with poorly regulated combustion processes. They are relatively small and their environmental impact is limited when processes are correctly managed.

Most air emissions of metal particles by refineries are directly related to fuel oil combustion. Emission control techniques to reduce SO_2 and PM both also serve to reduce metal particles (e.g. nickel) to air. Therefore these will not be treated separately in this report.

Other possible pollutants not considered, or outside of the scope of this document are:

- Hydrogen sulphide (H_2S)
- Hydrogen fluoride (HF).

H_2S and HF emissions are controlled such that under normal conditions of operation there are no detectable emissions. A large array of emergency controls and procedures are in place to avoid releases in case of abnormal operation conditions.

II.1.2. SOURCES

Air pollutants from refineries mainly originate from:

- For Carbon Dioxide:
  - Process furnaces, boilers, gas turbines
  - Fluidised Catalytic Cracking (FCC) regenerators
  - Flare systems
  - Incinerators
- For Sulphur Dioxide:
  - Process furnaces, boilers, gas turbines
  - Fluidised Catalytic Cracking regenerators
  - Sulphur Recovery Units (SRU)
  - Flare system
  - Incinerators
- For Oxides of Nitrogen:
  - Process furnaces, boilers, gas turbines
  - Fluidised Catalytic Cracking regenerators
  - Incinerators
- For Particulates:
  - Process furnaces and boilers, particularly when firing liquid fuels
  - Fluidised Catalytic Cracking regenerators and CO boilers
  - Coke plants
  - Incinerators
- For Volatile Organic Compounds:
  - Storage and handling facilities
  - Oil/water separation systems
  - Fugitive emissions (flanges, etc.)
  - Vents

According to the published CORINAIR database shown in **Appendix II Table A II-1** for the pollutants discussed, the contribution of refineries to the total European anthropogenic emissions is limited.

In **Table A II.2** the relative contribution to SO_2 and NO_x emissions from the different process units is given as a percentage of the total SO_2 and NO_x emission from refineries. Heaters and boilers contribute more than 60%.

II.2. CARBON DIOXIDE (CO_2)

II.2.1. SOURCES AND EMISSION OF CO_2

Fossil fuels consist mainly of carbon and hydrogen in varying proportions. Their combustion therefore results in the emission of carbon dioxide CO_2 and water vapour H_2O.

The supply of fuels to satisfy the energy demand of society is one of the main objectives of crude oil refining. As this process is energy intensive in itself a certain amount of the fuels produced by a refinery is consumed as refinery fuel.

According to the options and limitations described in **Section II.7** (Energy and Fuel Management) each refinery has its specific fuel pattern. This fuel pattern affects the CO_2 emissions of a refinery. Nevertheless all fuels produced in a refinery need to be balanced between the refineries own use and the fuels sold. However, globally the overall CO_2 emissions will remain constant.

CO_2 is a necessary component of biological life and, at normal levels, has no negative effects on health, vegetation or materials. With respect to its contribution to the Global Climate Change effect and sustainability, a decrease in CO_2 emissions from fossil fuel combustion is sought in the Kyoto Protocol.

The use of gaseous or liquid fuels for plant operation and some refinery processes, include:

- catalytic cracking
- hydrogen production
- catalyst regeneration
- sludge incineration
- utilities

These are sources of the CO_2-emissions of the refining industry. Calculated emission factors for CO_2 for various refinery fuels are presented below:

Table II.2 Emission Factors for CO_2

Fuel Type	Typical Composition	kg CO_2 / kg fuel	kg CO_2 / GJ
• Fuel gas	30% H_2/ 35% C_1/ 35% C_2	1.99	43
• Natural gas	100% methane	2.75	56
• LPG	50% C_3/ 50% C_4	3.02	64
• Distillate Fuel oil	60% P/ 10% O/ 30% A	3.22	74
• Residual Fuel	50% P/ 50% A	3.26	79
• Coke	90% C/10% H	3.63	117
(abbreviations: Carbon, Hydrogen, Paraffins, Olefins, Aromatics)			

II.2.2. CO_2 EMISSION CONTROL OPTIONS

Unlike SO_2 or $NO_{x,}$ treatment of flue gases as a feasible abatement technology for CO_2 is not available. Options for the refiner to reduce CO_2 emissions are:

- rational energy use
- use of fuels with high hydrogen contents.

Rational energy use means:

- Improving heat exchange between refinery streams
- integration of refinery processes to avoid intermediate cooling of components
- recovery of waste gases and their use as fuels (e.g. flare gas recovery)
- use of the heat content of flue gases.

Rational energy use also needs good operation to maximise heat recovery and process control (e.g.: O_2 excess, heat balances between reflux, product temperature to storage, equipment survey and cleaning). To get optimum results repeated operator training and clear instructions are necessary.

All these options are eventually restricted by physical or economic limitations.

It should be borne in mind, however, that some abatement techniques (e.g. Flue Gas Desulphurisation FGD) may be significant energy users, and therefore emitters of CO_2, and this is a disadvantage which needs to be set off against the advantages of the reduction sought.

II.2.3. CONSTRAINTS FOR CO_2 EMISSION REDUCTION

The political drive to reformulate fuels with the aim of reducing emissions from hydrocarbon fuel during their use has as a consequence that new refinery units are required. Additional processing units increase the fuel consumption of a refinery. The requirements to alter transport fuel quality for environmental purposes, such as:

- deep desulphurisation of gasoline and diesel fuel
- total aromatics reduction in these fuels
- decrease of the specific gravity or heavy ends
- increase of the cetane number of diesel fuel

do not increase refinery output, but require additional fuel use in new units.

Moreover, reducing aromatics in gasoline will decrease the reformer utilisation, which will result in hydrogen shortage. As a consequence, new hydrogen generation facilities necessary will again increase the CO_2 emissions for the same refinery throughput. This underlines the need for policy makers to strike a balance between new environmental fuel requirements and CO_2 abatement policy.

The successful energy saving efforts of the past years could be nullified by additional process requirements (thus additional CO_2 emission) for reformulated fuels. For example a study by CONCAWE [2] has shown that 10 kilograms of CO_2 are emitted for every kilogram of sulphur extracted from a product. These CO_2 emissions increase to much higher levels as product sulphur specifications decrease further.

II.2.4. EMERGING TECHNOLOGIES IN CO_2 ABATEMENT

Unlike the abatement of other pollutants no feasible technology exists for the removal of carbon dioxide from flue gases. A number of disposal options are however under scientific consideration. Due to technical, ecological and economical aspects a viable solution is not yet available.

Emerging technologies under consideration are

- disposal in the deep ocean
- disposal in deep aquifers
- disposal in exhausted oil and gas reservoirs
- disposal as a solid in an insulated repository

The ecological problems include the influence on the biological environment of the injection areas and the possible re-escape of the gas into the atmosphere. Whatever option is considered it will in itself consume energy and contribute to the emission of carbon dioxide.

An accurate comparison of the four approaches is however difficult. No doubt, solidification of CO_2 requires currently most energy and investment. According to a study of the IEA (1) the disposal costs for the approaches are:

Table II.3 Disposal Costs(1) for CO_2

	Ocean(2)	Aquifers(2)	Gas Reservoirs(2)	Solid
Cost (EUR/t C.)	3.4	3.9	6.8	500

(1) IEA Greenhouse Gas R&D programme
(2) Please note that only injection costs are reflected. These are only part of the overall investment and operating cost required.

II.3. SULPHUR DIOXIDE (SO_2)

II.3.1. SOURCES OF SO_2

SO_2 emissions result from the combustion of sulphur containing fuels. Most refinery processes require heat. This may be provided by steam or by a furnace. The fuel required for the raising of steam, or for the firing of the furnaces, originates either from natural gas that is bought from outside the fence or from fuel that is raised by the refinery itself, or a combination of both. The refinery fuels are the by-products of the refinery processes. The composition and quality of these fuels, both gaseous and liquid fuels, vary with the crude oils processed. Generally speaking, the refinery fuel pool is a careful balance between energy required, type of crude processed, emission limits and economic optimisations.

All crude oils contain sulphur compounds. Consequently, when firing refinery fuels, SO_2 will be emitted. There is a direct relation between the sulphur content of the fuel and the amount of SO_2 emitted. Pipeline quality natural gas normally contains only traces of sulphur compounds.

CONCAWE made a study of the SO_2 discharged to atmosphere from 70 refineries in the year 1995[2]. In this report the sources of SO_2 emissions are mentioned. As can be seen from **Table II.4**, the largest source of SO_2 emission, some 60%, is the SO_2 emitted by fuel fired. SO_2 emissions from FCC units are related to the sulphur present in the Cat. Cracker feedstock, and it is emitted during the catalyst regeneration process. The last step in the Sulphur Recovery Unit is an incineration step of the H_2S that is not converted to elemental sulphur. SO_2 emissions from the flares depend on the sulphur present in the fuel gas. ‘Miscellaneous’ includes flue gas from H_2S and sludge incineration, non-FCC catalyst regeneration, furnace de-coking and others (such as the safe start-up and shutdown of various facilities). These are both continuous and non-continuous sources of SO_2 emissions. The number of sources may vary from refinery to refinery, but the volume per source is relatively small.

In the sections below, the focus will be on the first three sources of the SO_2 emissions: decreasing the sulphur content of the fuel, an analysis of BAT for FCC units, and a description of the Sulphur Recovery Unit (SRU) process.

Table II.4 SO_2 Discharged to Atmosphere as an Average from 70 European Refineries

	SO_2 discharged expressed as sulphur (kt/y)	Percentage of refinery SO_2 emissions (%)
Fuel fired in furnaces/boilers	257	59.4
FCC units	58	13.5
Sulphur Recovery Units	46	10.7
Flares	22	5.0
Miscellaneous	49	11.4
	432	100

Source: CONCAWE Report 3/98[2]

II.3.2. DECREASING THE SULPHUR CONTENT OF THE FUEL

Since fuel combustion is the main source of SO_2 emissions of a refinery, abatement techniques should be focused on the fuel. Given that there is a direct relation between the sulphur content of the fuel and the SO_2 emissions, abatement techniques consist of two types: (1) decreasing the sulphur content of the fuel or (2) flue gas desulphurisation.

A decrease of the fuel sulphur content can be achieved by a (partial) switch to natural gas, a (partial) switch to low sulphur crude oil and refinery fuel desulphurisation. The first two options generally do not require large investments; the costs are operational costs related to the difference in costs for high sulphur and low sulphur crudes and fuels. When a connection to a natural gas grid is not readily available, a switch to low sulphur crude oils is the only low capital investment option.

The refinery fuel gas consists of C_1 to C_5 components and hydrogen. The gases come from different sources and are pooled in the refinery fuel gas system. Depending on the type of crude processed, the sulphur content of the untreated gas varies. Desulphurisation is achieved by amine scrubbing.

The liquid refinery fuel often consists of heavy residues, in which the sulphur of the crude is concentrated. Theoretically speaking it is possible to treat the liquid fuel in a hydrotreating process in order to remove the sulphur. However, because of the heavy fractions present in the liquid refinery fuel, much energy and large investments would be required (**Section II.3.3**; FCC Feedstock Desulphurisation).

Therefore, in most refineries a balance is made between the type of crude processed (high sulphur/low sulphur), the refinery fuel gas, natural gas and liquid refinery fuel. The ratio between these depends on local circumstances such as: the refinery complexity and the production of fuel gas, an outlet to a chemical complex for the fuel gas and/or LPG recovery.

II.3.3. BAT FOR SO_2 CONTROL ON FCC UNITS

In a Fluidised Catalytic Cracker (FCC) process, heavy feedstock is cracked and upgraded to valuable products such as LPG, gasoline blending components, gas oil and fuel oil. A by-product is the gas produced, which is sent to the refinery fuel system.

During the process, coke is deposited on the catalyst, which is burnt off in the regenerator. The exhaust gases of the regenerator are sent to atmosphere. This is the source of SO_2 and NO_x emissions from the FCC process.

The sulphur in the feed to the FCC is split between liquid product streams, H_2S in the gaseous products and SO_2 emission from the regenerator in the approximate ratio of 50/45/5.

In **Table II.5** a summary is given of the BAT for SO_2 emission control of FCC units. These techniques include; de-SO_x catalyst additive, feed desulphurisation and regenerator flue gas desulphurisation.

De-SO_x catalyst additive

This is an additive to the FCC catalyst that binds the SO_x compounds in the regenerator. In the reactor section this sulphur-metal compound is converted into H_2S, which is then further treated in the product gas stream. The amount of SO_x removed is dependent on the amount of De-SO_x additive added to the unit; removal efficiency is typically 30 - 50 %. There are no major investment costs required for this option, save for the dosing equipment of the additive to the catalyst system.

FCC feedstock desulphurisation

In a feed desulphurisation unit, sulphur is removed in a hydrotreating process. Hydrogen and energy are required for this process. As a result, the product streams of an FCC unit have a lower sulphur content. The sulphur removal efficiency depends on the boiling range of the FCC feed. The heavier the feed, the more energy is required for the same sulphur removal efficiency. This option is the most expensive one of the three mentioned here, and seldom used for FCC SO_2 reduction as the only driver.

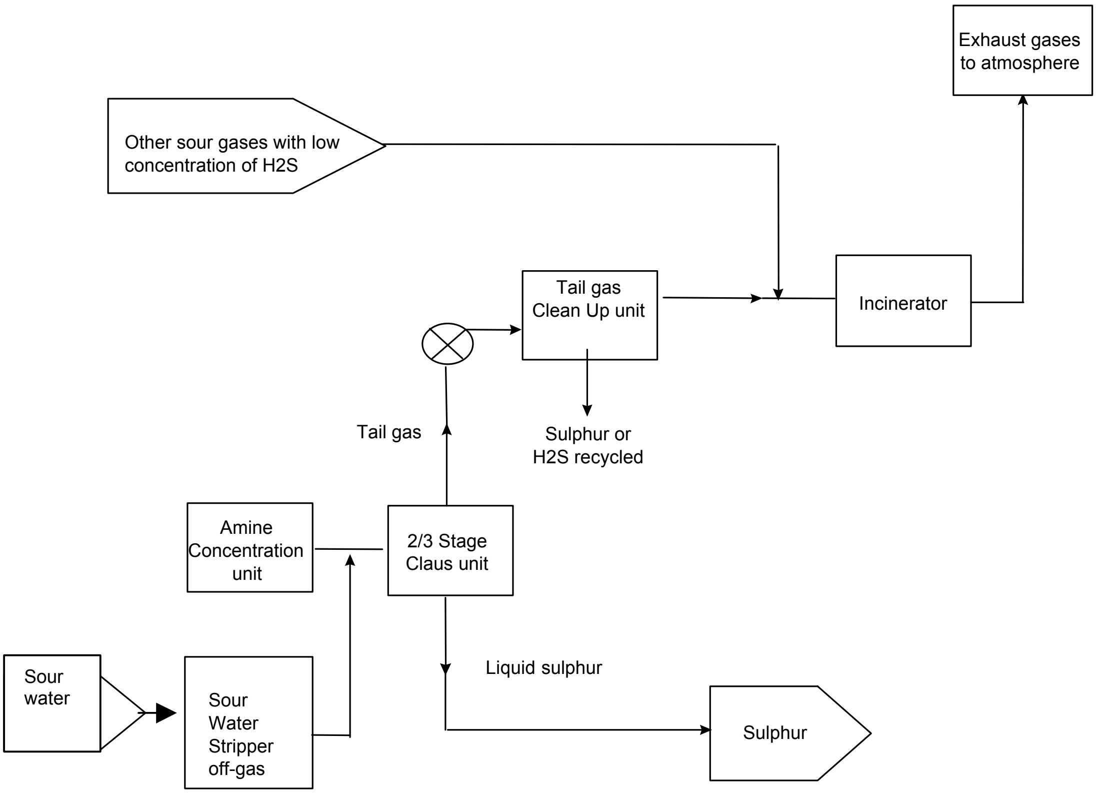
Flue gas desulphurisation

Most flue gas desulphurisation systems (FGD) use an adsorption or an absorption technique for the removal of SO_2, either regenerative or non-regenerative. These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide etc.. This is a hurdle for FCC applications and may require a gas cleaning system upstream of the FGD. The SO_2 removed from the gas phase will have to be further treated or disposed of. This can have an impact on the H_2S treating facilities or may generate an additional waste stream. Systems for flue gas desulphurisation are rarely applied on other refinery units than FCC regenerators.

II.3.4. SULPHUR RECOVERY UNITS (SRU)

Hydrogen sulphide (H_2S) rich gas is produced in different conversion and treating processes in a refinery. It is concentrated, using an amine scrubbing process. An H_2S rich sour gas is usually sent to a Sulphur Recovery Unit. Quite often, sour water stripper offgas is also sent to the SRU. **(see Fig. II.1)**

Figure II.1: General Sulphur Recovery System in refinery



The basic chemical reactions in a SRU are:

(1) $H_2S + 3/2\ O_2$ -> $SO_2 + H_2O$ (mainly in the combustion furnace)
(2) $2\ H_2S + SO_2$ -> $3/2\ S_2 + 2\ H_2O$ (mainly in the reactors)

There exist to-day alternative technological routes used to recover sulphur from H_2S sour gases; most of them on a similar principle of partial oxidation and reaction between sulphur dioxide and hydrogen sulphide.

A sulphur recovery unit is characterised by its global yield in terms of sulphur recovery (sulphur recovery efficiency):

$$\text{Yield (\% mass)} = \frac{\text{Liquid sulphur production}}{\text{Sulphur content of the feed}} \times 100$$

Typical sulphur recovery efficiencies of a two-stage sulphur recovery unit are in the range of 94 - 96 % (**Table II.6)**.

When the gas flow is (much) lower than 50% of the specified design parameters, the yield will decrease: consequently the sulphur emissions may increase.

When sour water stripper off-gas is processed in the SRU, care should be taken that the reaction temperature is above 1250°C, in order to ensure proper ammonia destruction.

Another important parameter is the reliability of the equipment because, if the SRU were out of use and the operation of the remainder of the refinery continued unchanged, there would be additional emissions of SO_2. However much work has been done in the past to increase the reliability of the SRUs.

Some refineries have, therefore, two or more SRUs installed. Normally they operate under shared load. If one unit is shutdown for any reason the majority of its load can be switched to the other running unit minimising the increase in emissions. If required, changes can then be made to the main process units to reduce the quantity of H_2S produced.

H_2S rich gas can also be sent to other processes. Especially low flows of gases containing low H_2S concentrations sometimes can be treated better in other processes such as Sulpherox©. The determining factors to choose another process are reliability, product sulphur quality economics and the required sulphur recovery.

Emission limits for a Sulphur Recovery Unit should take into account the two parameters in addition to its capacity:

- yield
- availability

With the exception of CO_2 and less than 50 ppm NO_x in the flue gas from the combustion furnaces, there are no other notable emissions from the SRU other than SO_2.

Technologies to prevent / reduce emissions

Tail gas from a Sulphur Recovery Unit contains sulphur oxides and hydrogen sulphide, totalling 5 % of total sulphur intake for a plant with a yield of 95 %. For a production of 30 000 tons of sulphur per year, sulphur emissions are 1580 tons (or 3160 tons SO_2) see **Table II.6**.

Improvement of the yield and consequently reduction of sulphur emissions can be obtained through two principal technologies and/or a combination of them:

- addition of a third reactor.
- addition of a Tail Gas Clean-up Unit (TGCU).

The following technologies are widely considered as the best available to prevent/reduce SO_2 emissions.

The addition of a “SCOT” unit to a two or three stage SRU achieves at design conditions a sulphur recovery efficiency in the range of 98-99.99 %. In a SCOT unit the Claus tail gas is selectively hydrogenated to H_2S, which is separated from the gas stream in an amine absorber. The loaded amine is routed to a regenerator where H_2S is stripped off and routed back to the Claus unit. A so-called “stand-alone SCOT” has its own amine stripper column, while in a cascaded SCOT the loaded amine of the SCOT absorber is recombined with other amine streams and regenerated in a common column.

In a “Super Claus” process, the tail gas is led through a reactor with a selective oxidation catalyst, which converts H_2S with excess oxygen to sulphur.

The “Clauspol” process is based on the Claus reaction (hydrogen sulphide plus sulphur dioxide reacting to sulphur and water). The reaction takes place in a column with packed beds, with the gas entering from the bottom of the column while a solvent with catalyst is distributed in the top of the column. The sulphur is collected at the bottom of the column.

The “Sulfreen” process is also based on the Claus reaction. Here the sulphur produced is adsorbed on an active alumina based catalyst. Two reactors are used, while one is in the adsorbing mode, the other reactor is regenerated by stripping off the sulphur.

The “Hydro Sulfreen” process is a Sulfreen process with a pre-treatment step. The pre-treatment step consists of the conversion of COS and CS_2 to H_2S, followed by the Claus reaction.

The “CBA/Amoco” cold absorption process is very similar to the Sulfreen process, except in the fact that the CBA process uses a hot process stream indigenous to the Claus process to accomplish regeneration of the sulphur loaded catalyst bed. The hot process stream is part of the effluent of the first Claus reactor.

The “Sulpherox©.” process is a possible alternative to the Claus process. In this process the H_2S is converted to elemental sulphur through a reaction with aqueous iron, Fe^{+++}. Organic ligands or chelating agents are used to increase the solubility of iron in the operating solution. The spent iron chelate is regenerated by the reaction of Fe^{++} with air to Fe^{+++}. The solid sulphur produced can easily be filtered out.

II.3.5. EMISSION MONITORING (SO_2)

SO_2 emission analysers for direct monitoring are readily available on the market. A point of attention here is the robustness of the apparatus because of fouling which may occur in a flue gas duty.

Because there is a direct relation between the sulphur content of the fuel and the SO_2 emission, the SO_2 emission can also be monitored indirectly via the measuring of relevant process parameters. For instance one can calculate it from a continuous measure of the fuel consumption and sulphur content of the refinery fuel.
Indirect monitoring is much more cost effective than directly measuring the SO_2 content of flue gases.

Table II.5 Analysis of Best Available Techniques for SO_2 Control Fluid Catalytic Cracking

Example : Capacity of process: 1.5 Mt/y (FCC), 30 000 bpd
: Volume of gas: 10^9 m^3/y
Pollutant Initial concentration : 4 000 mg/m^3 (S in feed approx. 2.5%)
(These values may vary depending on feed and process)

NAME OF TECHNIQUE	DE-SO_X CATALYST	DISTILLATE FEED DESULPHURISATION (2)	RESIDUE FEED DESULPHURISATION (2)	FLUE GAS DESULPHURISATION	REGENERATIVE FGD	CAUSTIC SCRUBBING WET GAS SCRUBBER
EFFICIENCY	30-50%	UP TO 90%	UP TO 85%	90%	95-98%	UP TO 85%
TYPICAL DOWNSTREAM EFFLUENT	3 000 TO 1 300 mg/m ^{3}	DOWN TO 400 mg/m ^{3} DEPENDING ON FEEDSTOCK	DOWN TO 600 mg/m ^{3} DEPENDING ON FEEDSTOCK	400 mg/m ^{3}	200 TO 100 mg/m^3	DOWN TO 600 TO 100 mg/m^3 DEPENDING ON FEEDSTOCK
INVESTMENT EXPENSES	0(3)	80-100 M EUR(4)	200-300 M EUR	15-20 M EUR	24-28 M EUR	10 M EUR
OPERATING EXPENSES	0.05-0.1 EUR/bbl i.e. 1 M EUR/y	4-9 M EUR/y	15-25 M EUR/y	2-3 M EUR/y	1.5 M EUR/y	2-5 M EUR/y
OTHER IMPACT(5)	INCREASED ENERGY CONSUMPTION POSSIBLE. BOTTLENECKING OF H_2S HANDLING FACILITIES	INCREASED ENERGY CONSUMPTION. PRODUCTS WITH LOW SULPHUR CONTENT. CATALYST DISPOSAL. REDUCED NO_X EMISSION	INCREASED ENERGY CONSUMPTION. PRODUCTS WITH LOW SULPHUR CONTENT. CATALYST DISPOSAL. REDUCED NO_X EMISSION	INCREASED ENERGY CONSUMPTION. BY PRODUCT. RAW MATERIAL SUPPLY AND HANDLING	INCREASED ENERGY CONSUMPTION. POSSIBLE BOTTLENECKING OF H_2S HANDLING FACILITIES	WASTE WATER. (Na_2SO_4) REDUCED PARTICULATE EMISSION

Source: IFP, Hydrocarbon Processing, industry

NB: Operating costs include only cash direct operating expenses i.e. do not include (depreciation) of investment, nor financial charges
Investment costs refer to new plant installation (see section on retrofitting existing plants)

(2) These techniques will seldom be used for environmental purpose (see paragraph II.4.3)
(3) In some cases, amine treating capacity will have to be increased as well as the SRU capacity
(4) Excluding H_2 production and H_2S handling facilities
(5) Water used for the different FFC sections yields 20-40 m^3/hr of sour water

Table II.6 Analysis of Best Available Techniques for SO_2 Control
Sulphur Recovery Unit (Claus unit)

Example : Capacity of process: 30 000 t/y sulphur production (sulphur recovery efficiency 94 – 96% for a two stage unit)
: Volume of gas: 60 million m^3/y
Pollutant Initial concentration: 34 000 mg SO_2/m^3

NAME OF THE TECHNIQUE	3^{rd} REACTOR	STAND ALONE SCOT	CASCADED SCOT COMMON REGENERA-TOR	SUPER CLAUS	SUPER CLAUS + CLAUS STAGE	CLAUS - POL	SULFREEN	HYDRO-SULFREEN	CBA/AMOCO COLD REAL ABSORPTION
OVERALL EFFICIENCY (%)	98.6	99.9	99.8 – 99.95	98.5	99.2	99.6	99	99.5	99
INVESTMENT COSTS M EUR	2 – 3	7.7 15-20(1) 17(1)	8.5	3.0	4.5	14(1) 10	3(1) 10(1)	4(1) 9(1)	10-15
OPERATING COSTS M EUR/y	0.1	0.1	0.1	0.1 – 0.5	0.1 – 0.5	0.1	0.1 – 0.5	0.1 – 0.5	
COST EFFECTIVE-NESS EUR/ton SO_2	32	32	32	32 – 161	32-160	32	32-160	32-160	
OTHER IMPACT	NEGLIGIBLE	LOAD OF SRU INCREASED BY 8%	SRU LOAD INCREASED BY 8%. INCREASED ENERGY CONSUMPTION 1.2% OF THE FEED-						

II.4. NITROGEN OXIDES (NO_X)

II.4.1. SOURCES OF NO_X

NO_x emissions are considered as the sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2).

NO_x emissions from refineries depend on the fuel type, fuel nitrogen or hydrogen content, combustor equipment design, and operating conditions. Accordingly, large differences in the NO_x emission level can be expected between refineries and even within different combustion equipment at the same refinery at different times. Differences in temperature, residence time, and oxygen concentration result in varying levels of thermally formed NO_x. The influence of temperature is most important with NO_x emissions increasing exponentially with temperature.

As a first approximation, NO_x emissions are magnified by the use of hydrogen- and residual fuels containing fuel bound nitrogen. High hydrogen fuels result in higher flame temperatures, which lead to higher NO_x levels. Although all the fuel nitrogen does not end up as NO_x emissions, the fuel NO_x contributions can range from non-existent, as in the case of natural gas fuelled equipment, to several times the thermal NO_x contribution of the equipment for refinery fuels. Refinery gaseous fuels often contain nitrogen containing amines and other compounds. Liquid refinery fuels often have significant nitrogen content, especially if they are residues from the processing operations. Solid fuels, such as coke deposits on catalyst, also often have high nitrogen levels.

Accordingly, comparisons of alternate control technologies that might be considered for BAT must be by combustion equipment type and based on a defined but representative fuel.

While, as discussed above, the emissions from particular combustion equipment is variable, **Table II.7** provides general guidance on the uncontrolled NO_x levels, measured at customary reporting conditions, that can be expected from FCC regenerators, fired heaters, boilers and gas turbines. The wide variation in emission levels from the FCC regenerator reflects both the wide variations in nitrogen level in the feed to the FCC units, and the regenerator and waste heat boiler operating conditions. The fired heaters, boilers and gas turbines in the table are all fired with refinery blend gas leading to the narrow NO_x emission levels. These emission levels form the starting point for the control technique applications discussed in this document (**Table II.8**). The key issues for all NO_x controls are summarised in **Tables II.9 to 12**

Table II.7 NO_x Emission Ranges for Uncontrolled Combustion Equipment

FCC	**Fired Heaters & Boilers** (1)	**Gas Turbines** (1)
200-2 000 mg/Nm³ @ 3% O_2 (2)	75-400 ppm @ 3% O_2	160-510 ppm @ 15% O_2

(1) Fired heaters, boilers and gas turbines fuelled with refinery blend gas.

(2) FCC regenerator emission levels reflect the wide-range of fuel nitrogen that can be found in the FCC feed among units with different crude supplies and upstream process configurations.

II.4.2. NO_X EMISSION CONTROL TECHNIQUES

NO_x control techniques fall into four main categories:

- Pre-combustion operational changes
- Combustion modifications
- Post-combustion flue gas treatment
- Emerging technologies

Pre-combustion operational changes include de-nitrification of feed to fired heaters, to boilers and to FCC units. In FCC units a trade-off can be made between carbon monoxide emission levels (CO) and NO_x.

Combustion modifications involve changes to the combustion equipment or operating conditions that either lower the flame temperature or change the concentration of reactants to minimise NO_x formation. They include: low NO_x combustors; either low NO_x burners or dry low NO_x combustors for gas turbines; flue gas recirculation (FGR) or steam diluent injection and de-NO_x additives for FCC regenerators.

Post-combustion techniques include Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR). SNCR and SCR have been used for large boilers and for gas-fired refinery heaters. Neither of the post-combustion techniques have been applied to fired heaters in European refineries. While application of these techniques may be considered for entirely new gas-fired heaters, design and space considerations, as pointed out in Part I, may make retrofit impossible. Since there is no experience with SCR on heavy-oil-fired refinery heaters and the experience with SNCR on oil-fired heaters is at best limited, the application of post-combustion techniques to the residual-oil-fired heaters that are prevalent in European refineries remains an emerging technology. A pilot unit to evaluate SCR on a heavy-oil fired heater is currently underway at a Dutch refinery. Some of the post-combustion techniques can be used either alone or in combination.

These control techniques and the specific combustion equipment needing control suggest that the following NO_x control combinations be considered (**Table II.8**) . As the discussions indicate, not all of these combinations are either practical or cost-effective for the entire range of fuel-types and combustion equipment-types found in refineries.

Table II.8 Technologies to be Analysed

	Specific Functions	**Interfunctional Aspects - Fuel Management**		
	FCC	**Boilers**	**Gas Turbines**	**Fired Heaters**
NO_x	• SNCR • SCR • NO_x Removal Additives • CO Promoter Optimisation	• Flue Gas Recirculation • Ultra Low NO_x Burners • SNCR • SCR • Low NO_x Burners plus SCR	• Dry Low NO_x Combustors • Steam Injection • SCR • Steam Injection plus SCR • Low NO_x Combustors plus SCR	• Low NO_x Burners • Ultra low NOx Burners • SCR • SNCR

II.4.3. DESCRIPTION OF NO_X CONTROL TECHNOLOGIES

Pre-Combustion Approaches

Fuel De-Nitrification

The use of by-product and residual streams to meet the fuel requirement of fired heaters, boilers and gas turbines is not only cost-effective, but also is environmentally beneficial in that it makes use of what otherwise would be a waste refinery stream that would be flared without recovering the energy content. Cleaner burning fuels, e.g., natural gas, could replace these by-product and residual streams, thereby reducing NO_x at a specific combustion unit, but leaving a waste product still to be disposed of.

The nitrogen content of the feed to the FCC is determined by the crude that is used at the refinery and by the process units upstream of the FCC unit. Feed hydrotreating can reduce the feed nitrogen content, which in turn reduces the fuel nitrogen content on the coke burned in the regenerator, substantially decreasing fuel NO_x. However, the severe hydrotreating required is very expensive and energy intensive and is normally only done to meet required fuel specifications.

CO Promoter Optimisation

FCC regenerators are operated either in a complete or partial combustion mode. In the partial combustion mode considerable CO is present in the flue gas and it is consumed downstream of the regenerator in a CO boiler, both to capture the energy in the CO and to meet environmental requirements. In the full combustion mode there is no downstream environmental control for CO and a CO oxidation promoter is often added to the regenerator to catalyse the oxidation of CO. This promoter also catalyses the oxidation of the fuel nitrogen in the coke, increasing the NO_x levels.

Varying the amount of CO promoter used can reduce NO_x emissions at the expense of higher CO emissions.

Combustion Modifications

Diluent Injection

Inert diluents, such as flue gas, steam, water, or nitrogen, added to combustion equipment reduce the temperature and the concentration of NO_x producing reactants in the flame zone thereby reducing thermally formed NO_x.

Flue Gas Recirculation

External flue gas recirculation (FGR) is applied to boilers to increase the diluent effect, hence to reduce combustion temperature. Typically 20% of the available flue gas from the boiler stack is ducted to mix with fresh combustion air. In a boiler retrofit, FGR increases hydraulic loads, and shifts the heat load towards the convective section(s) and may not be practical. Safety considerations due to the possibility of explosion in the event of a tube burst make FGR impractical for fired heater applications.

Steam or Water Injection

This technique is widely applied to gas turbines both in new installations and retrofits and is also applicable to fired heaters and boilers. Within the refining industry, steam injection predominates. Capital cost is less than that of SCR, making the technology a good first choice for substantial levels of NO_x reductions, with SCR often added on if higher NO_x reduction is needed. Substantial recurring operating costs are however encountered for producing high purity steam, and also maintenance costs for re-blading may be high.

Nitrogen Injection

By-product nitrogen from the air separation plant in refinery residue gasification projects has recently been commercially demonstrated as a diluent for gas turbine NO_x reduction. While it may at first seem strange to add nitrogen to reduce NO_x, the added molecular nitrogen reduces the combustion temperature, thereby reducing thermal NO_x formation.

Low NO_x Burners

Low NO_x burners, either air staged or fuel staged, have the aim of reducing peak temperature, reducing oxygen concentration in the primary combustion zone and reducing the residence time at high temperature, thereby decreasing thermally formed NO_x. Staging of fuel addition is also thought to provide a reburning effect, further reducing the NO_x. The decreases obtained by low NO_x burners average around 40%. Ultra-low NO_x burners add internal recirculation of flue gases to the features of the low NO_x burner, enabling NO_x reductions of 75 % or better. Application is straightforward for new installations of both fired heaters and boilers. Retrofitting of low NO_x burners depends on the furnace design and may be simple, difficult or impossible due to the increased flame volume, i.e. the flame size is too large for the size of the radiant box. In many cases retrofitting requires major changes to the furnace floor structure and controls that add greatly to the capital cost. This substantially increases the cost per unit of NO_x removed, thus reducing the cost effectiveness of this technique. For new installations capital expenditure may be higher, but operating and maintenance costs of low NO_x burners are comparable to that of standard burners.

Under the designation dry low NO_x combustors, low NO_x combustors have achieved 90% reduction in NO_x emissions in natural gas fired gas turbine applications. They are used either alone or with add-on SCR. Low NO_x combustors are not available for gas turbines fired with refinery blend gas that contains more than 5 to 10 volume percent of hydrogen.

Post-Combustion Approaches

The post-combustion approaches work on the flue gas produced in the combustion process, reducing the NO_x to nitrogen gas. In theory they are potentially applicable to reduction of NO_x from any combustion device. Generally they can give the same percentage reduction in NO_x regardless of the starting concentration of NO_x, although in practice the percentage NO_x reduction drops-off at starting NO_x concentration levels below 50 mg/Nm^3. In addition, the NO_x destroying reactions are only operable within a limited temperature window.

The currently available post-combustion techniques use ammonia or ammonia derivatives as a reactant which can result in ammonia slip and ammonium sulphate salt formation. Ammonia slip is unreacted ammonia that can lead to NO_x formation and water pollution downstream of the source. Ammonium salt formation can lead to heater exchange equipment fouling, thereby limiting the maximum sulphur oxide flue gas level and minimum stack temperature that can be used with these techniques.

Selective Non-Catalytic Reduction (SNCR)

SNCR is a non-catalytic process for removing oxides of nitrogen from the flue gas by gas phase reaction of ammonia or urea at high temperature, i.e. around 950°C. The reactant is injected through multiple nozzles into the radiant or convection section of process furnaces and boilers. To achieve good mixing, the small amount of reactant is injected along with a carrier gas, usually air or steam. NO_x reductions up to 60% have been demonstrated, if the flue gas temperature is as per design. At lower or higher than design loads however, the effectiveness decreases. Cost considerations include the initial capital costs for modifying the furnace or boiler, piping to inject the reactant, the reactant supply system and a recurring cost for ammonia or urea to react with the NO_x.

Selective Catalytic Reduction (SCR)

The SCR process removes nitrogen oxides by reaction of ammonia vapour with the flue gas over a catalyst bed where NO_x is reduced to nitrogen and water vapour. Catalysts are available to achieve a high level of NO_x reduction in narrow temperature windows from 250 to 550 °C. This greatly increases the flexibility of SCR for retrofit applications. However, considerable plot space is needed for its installation, often making SCR impractical or cost ineffective for retrofit installations. Capital investment includes the structure to hold the catalyst and the cost of the catalyst. Additional charges for retrofit applications include the cost of structural modifications and ductwork. Like SNCR, an ammonia injection and supply system and a recurring cost for ammonia to react with NO_x is required.

SCR can achieve near 90% reduction of NO_x except at very low NO_x concentrations, where NO_x reduction is typically about 75%. It can be employed as an additional control technology following initial NO_x reduction by low NO_x burners, steam injection or SNCR.

Emerging Technologies

SCR for Oil-fired Heaters

SCR has been successfully applied to high sulphur and gas streams with high particulate content in the coal-fired utility industry and FCC units. Application of SCR to the combination of high sulphur and sticky soot containing gas streams, characteristic of residual oil firing in refineries, is however still a non-commercial technology.

SNCR on Oil-fired heaters

Experience with SNCR on oil-fired heaters is at best limited; the application of post-combustion techniques to the residual-oil-fired heaters that are prevalent in European refineries remains an emerging technology. A pilot unit to evaluate SCR on a heavy-oil fired heater is currently underway at a Dutch refinery.

Low NOx Additives

NO_x removal additives are an emerging technology that may have future applicability for NO_x control from FCC regenerators. The additives are added to the regenerator of the FCC to promote the destruction of NO_x by reaction of nitrogen oxides with carbon monoxide or coke. They are often specially promoted SO_x removal additives, providing the ability to simultaneously reduce the NO_x and SO_x emissions from the FCC regenerator. They have been investigated under laboratory conditions but have not been commercially demonstrated. These additives are attractive since they need no capital investment, although the operating cost for additive replacement is expected to be large.

II.4.4. COST OF NO_X CONTROLS

The capital cost of NO_x control installations used in this analysis is the total erected cost (TEC). In addition to the cost of purchased control equipment from the vendor, TEC includes engineering costs, installation costs and contingency. Normally the purchased equipment cost is only about 20 to 25% of the TEC. The annual operating cost used in this analysis includes the direct and indirect operating costs and a 15% per annum capital charge.

For this analysis natural gas or a refinery blend gas has been chosen as the base fuel for comparison of NO_x control technologies for fired heaters, boilers and gas turbines. The blend contains approximately 50 volume percent methane, about 25 volume percent C_2 to C_4 compounds and the remainder is hydrogen. It is representative of the type of gaseous fuel that might be fired in a refinery and has an uncontrolled NO_x emission comparable to that of distillate firing, but 50% higher compared to natural gas firing. Firing low-Joule gas or fuels containing chemically bound nitrogen compounds would result in lesser or greater quantities of uncontrolled NO_x respectively. Any changes in uncontrolled NO_x levels would impact primarily the cost effectiveness (EUR per ton of NO_x reduction) of specific control technologies.

Table II.9 NO_x Control for Fired Heaters and Boilers Firing Refinery Blend Gas

Basis: 100 Giga joules/hr installation
Retrofit of existing unit
Refinery blend gas firing
Uncontrolled NO_x emissions of 150 ppm at 3% oxygen (300 mg/Nm^3)

	Flue Gas Recirculation plus Low NO_x Burner (6)	Ultra Low NO_x Burners	SNCR	SCR	Ultra Low NO_x Burner plus SCR
Reduction Performance (1) NO_x reduction %	70	75	60	90	90+
Down to ppm @ 3% O_2	45	30	50	15	10
Investment Cost (1998) (5) (M EUR)	0.9 (3)	0.2-0.6 (2)	0.4-0.5 (2)	2.8-3.2 (2)	3.0-3.5(2) 2.1 (3)
Operating Costs per year (5) (excludes capital charge) (M EUR)	0.08	nil	0.025 (2)	0.15 (2)	0.15 (2) 0.26 (3)
Cost Effectiveness EUR/ton NO_x Removed (incl. capital charge @ 15%)	2 000-4 300 (3)	650 (1) 600-700 (2) 1 700-5 000 (4)	2 000-2 500 (2) 1 800-4 300 (4)	8 300-9 800(2) 12 000 (3) 4 200-9 000 (4)	9 100-10 500 (2) 9 000(3)
Other Impacts	Add energy for fans	None	Energy to produce NH_3, risk of NH_3 emissions, turn down is a problem	Energy to produce NH_3, risk of NH_3 emissions, catalyst disposal	Energy to produce NH_3, risk of NH_3 emissions, catalyst disposal

(1) U.S. Environmental Protection Agency RBLC clearinghouse listing and California Air Resources Board BACT listing. These listings provide the permitted emission levels in permits granted within the United States or the State of California for alternative control technologies to meet RACT, BACT (Best Available Retrofit Control Technology) and LAER (Lowest Achievable Emission Requirements.) The listings cover the period to 1996.

(2) Alternative Control Techniques Document—Control of NO_x Emissions from Process Heaters, U.S. Environmental Protection Agency, EPA-453/R-93-015, February, 1993

(3) Proprietary industry studies

(4) CONCAWE Member Company Information

(5) Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/y have been used in this analysis.

(6) Flue gas recirculation (FGR) is not available for fired heaters due to safety considerations

Table II.10 NO$_x$ Control for Fired Heaters / Boilers Firing Residual Fuel Oil

Basis: 100 Giga joules/hr installation
Retrofit of existing unit
Residual Oil firing
Uncontrolled NO$_x$ emissions of 250 ppm at 3% oxygen (500 mg/Nm^3)

	Boilers			Heaters
	Low NO$_x$ Burners (3)	SNCR	SCR	Low NO$_x$ Burners (3)
Reduction Performance (2) NO$_x$ reduction %	40	60	75	40
Down to ppm @ 3% O$_2$	150	100	65	150
Investment Cost (1998) (1) (M EUR)	0.3-0.9 (2)	0.4-0.9 (2)	2.4-3.4 (2)	0.3-0.9 (2)
Operating Costs per year (1) (excludes capital charge) (M EUR/year)	Nil-0.02 (2)	0.05-0.07 (2)	0.1-0.2 (2)	Nil-0.02 (2)
Cost Effectiveness EUR per tonne NO$_x$ Removed (incl. capital charge @ 15%)	500-1 800	1 500-2 800 1 500-4 300 (4)	5 000-8 000 4 500-10 200 (4)	500-1 800
Other Impacts	None	Energy to produce NH$_3$, risk of NH$_3$ emissions	Energy to produce NH$_3$, risk of NH$_3$ emissions, catalyst disposal	None

(1) Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/y have been used in this analysis

(2) Alternative Control Techniques Document—Control of NO$_x$ Emissions from Process Heaters, U.S. Environmental Protection Agency, EPA-453/R-93-015, February, 1993

(3) ULNB are not available for oil-fired fired heaters and boilers.

(4) California Clean Air Act Guidance, *Determination of RACT and BARCT (Best Available Retrofit Control Technology)*, California Air Resources Board, July 1991

Table II.11 NO$_x$ Control for Gas Turbines Firing Natural or Refinery Blend Gas

Basis: 85 MW output turbine (representative of a GE Frame 7 size unit) (electrical output)
Natural gas or refinery blend gas firing
Uncontrolled NO$_x$ emissions of 250 ppm at 15% oxygen (350 g/GJ)

	Dry Low NO$_x$ Combustors	Steam Injection	SCR	Steam Injection plus SCR	Dry Low NO$_x$ Combustors plus SCR
Fuel fired	Natural gas (8)	Refinery blend gas	Refinery blend gas	Refinery blend gas	Natural gas (8)
Reduction Performance (1) NO$_x$ reduction %	90	80-90	90	98-99	98
Down to ppm @ 15% O$_2$	25	25-42	25	3-6	5
Investment Cost (1998) (4) (M EUR)	2.2 (2)	3.4 (5)	5.4 (3) 4.9 (2)	8.3 (2)	7.2 (2)
Operating Costs per year(4) (excludes capital charge) (M EUR)	Nil	0.8 (2)	1.3	2.1 (2)	1.2 (2)
Cost Effectiveness EUR/ton NO$_x$ Removed (includes capital charge @ 15%)	350 (2)	1 500 (2)	1 700-8 000 (3)	3 800 (6) 3 600 (3)	7 600 (7)
Other Impacts	none	Energy to produce steam, higher emissions of CO and hydro-carbons	Energy to produce NH$_3$, risk of NH$_3$ emissions, catalyst disposal	Energy to produce NH$_3$, risk of NH$_3$ emissions, catalyst disposal	Energy to produce NH$_3$ and steam, risk of NH$_3$ and higher CO emissions, catalyst disposal

(1) U.S. Environmental Protection Agency RBLC clearinghouse listing and California Air Resources Board BACT listing. These listings provide the permitted emission levels in permits granted within the United States or the State of California for alternative control technologies to meet RACT, BACT and LAER (Lowest Achievable Emission Requirements.)

(2) Alternative Control Techniques Document— NO$_x$ Emissions from Stationary Gas Turbines, U.S. Environmental Protection Agency, EPA-453/R-93-007, January, 1993

(3) Proprietary industry studies

(4) Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/y have been used in this analysis.

(5) Costs from Reference (2) above and includes investment costs for steam production.

(6) Costs from Reference (2) above for SCR increment only with NO$_x$ entry to SCR following steam injection of 42 ppm.

(7) Costs from Reference (2) above for SCR increment only with NO$_x$ entry to SCR following low NO$_x$ combustor of 25 ppm.

(8) Dry Low NO$_x$ combustors are not available for refinery blend gas containing more than 5 to 10% hydrogen

Table II.12 NO_x Control for Fluid Catalytic Cracking Units

Basis: 30 k bbl/day FCCU with CO Boiler
800 mg/Nm^3 uncontrolled NO_x emission [(3)]

	CO Promoter Optimisation	SNCR	SCR	Feedstock Hydrotreating
Reduction Performance NO_x Reduction %	30	60	85	Up to 85
Down to mg/Nm3@ 3% O_2	560	320	120	120
Investment Cost (5) (M EUR)	Nil	5.4 (1)	6.3 (2) 11-13 (1)	80-100 (6)
Operating costs per year (5) (M EUR)	NA	0.1	0.4-0.8 (1)	4-9
Cost Effectiveness EUR/ton NO_x Removed (includes capital charge @ 15%)	NA	1 900	2 800-3 300	28 000 (4)
Other Impacts	Higher CO emissions	Energy to produce NH_3, risk of NH_3 emissions	Energy to produce NH_3, risk of NH_3 emissions, catalyst disposal	Energy to produce H_2 for hydrotreating, reduced SO_x emissions, catalyst disposal

NA = Data is not available to calculate a value. Cost will be very dependent on how CO promoters are used in the operation of the regenerator.

(1) Proprietary industry study.
(2) Capital cost based on calculated flow rate with the same SCR cost per unit flow as for fired heaters and gas turbines.
(3) Removal of NO_x from FCCU regenerator vent gases, Refining, PTQ Spring 1997. Analysis of SCR installation at Scanraff refinery, Lysekil, Sweden.
(4) Assigns all feedstock hydrotreating costs to NO_x control.
(5) Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/y used in this analysis.
(6) UFIP submission for STF-55 study, 23 July 1998

II.4.5. NO_X EMISSION MONITORING

Once installed, emission control techniques are monitored for compliance. In addition to periodic flue gas sampling normally required by regulations, continuous emission monitoring systems (CEMS) are sometimes required. Historically, such monitoring has been done using NO_x specific analysers in the CEMS. Recently, predictive emission monitoring systems (PEMS) have been demonstrated to be accurate and reliable monitoring devices and have begun to be accepted by regulatory authorities as an alternative analyser.

PEMs make use of existing process sensors already installed at the facility for operational and other environmental compliance measurements, along with an understanding of how these measurements affect NO_x emissions, to predict NO_x

emission levels. Using existing process sensors provides a more cost-effective approach than continuous measurement of NO_x emissions.

In the case of NO_x monitoring, PEMS would likely include measurements of air preheat temperature, furnace operating temperature, fuel hydrogen content, oxygen concentration in the flue gas and ambient humidity.

II.5. VOLATILE ORGANIC COMPOUNDS (VOCs)

II.5.1. SOURCES OF VOCs

The main sources of VOCs from refineries are fugitive emissions from piping systems, waste water systems, storage tanks, loading and unloading systems.

II.5.2. FUGITIVE EMISSIONS FROM PROCESS UNITS

Overview

Fugitive emissions from process equipment are the largest single source of VOCs emitted to the atmosphere in a refinery and can frequently account for 50% of the total emissions. Fugitive emissions embrace the emissions that occur from items such as valves, pump and compressor seals, flanges, vents and open ends.

Factors driving these releases of hydrocarbons are equipment design, quality of the sealing system, maintenance programme and properties of the line contents. Poorer designs (with wider tolerances), poor sealing systems (e.g. leak prone valve packings) and limited maintenance will lead to higher emissions.

Valves are considered to account for approximately 50-60% of fugitive emissions. Furthermore, the major portion of fugitive emissions comes from only a small fraction of the sources (e.g. less than 1% of valves in gas/vapour service can account for over 70% of the fugitive emissions of a refinery).

Some valves are more likely to leak than others such as:

- Valves that are operated frequently, such as control valves, may wear more quickly and will allow emission paths to develop. However, newer, low leak control valves provide good fugitive emissions control performance.
- Valves with rising stems (gate valves, globe valves) are likely to leak more frequently than quarter-turn type valves such as ball and plug valves.

LDAR

The first level of control for fugitive emissions is a Leak Detection and Repair (LDAR) Program. The main experience of LDAR programmes has been in the USA where since the early 1980s; the US Environmental Protection Administration (USEPA) has required implementation of LDAR under its New Source Performance Standards (NSPS).

The technique for LDAR is to measure the concentration of gas at the potential leak site on the piping component (under a prescribed procedure) and to effect a repair to the leaking item if a level of gas concentration equal to or greater than a regulatory leak definition concentration (10 000 ppm) is measured.

The critical factors in determining the cost effectiveness of an LDAR programme include:

- the definition of what constitutes a leak
- the frequency of the required inspections
- the level of record keeping required
- the components included in the LDAR programme
- the requirements concerning repair of “leaking” components

Judicious selection of the items above can result in a programme which returns significant fugitive VOC reductions at a EUR/t cost far below a programme that is very conservative in defining all the above items.

Experience has shown that refineries implementing annual LDAR programmes with monitoring and repair of components found leaking above 10 000 ppm can achieve fugitive emission reductions of at least 50% in the first year.

New data analyses published by the American Petroleum Institute (API) indicates that over 90% of reducible fugitive VOC emissions from only 0.13% of components (those screened at above 10 000 ppm) could be avoided. Some states in the USA have introduced a lower threshold (a leak definition of 100-500 ppm) to their LDAR programmes with a corresponding increase in the cost of implementation resulting in an order of ten fold increase in cost for a marginal increase in VOC reduction.

Flaring

Another control technique is to collect VOCs from vents, pumps and compressors and to route them to a flare system. This may be difficult and expensive to do in a retrofit situation. Costs are given in **Table II.13**.

Design consideration technologies

In order to limit volatile organic compound emissions, consideration should be given to the general design aspects given below:

- minimising the number of flanges.
- selection of valves with intrinsically low fugitive emissions either by manufacturer type and/or packing.
- pumps and compressors fitted with improved seals and sealing liquids where appropriate.
- providing pumps with sumps and drains connected to a closed system for the collection of spills.
- using closed-loop sampling systems and collection systems, with segregation of wet and dry oil waste streams.
- making process leak point sources e.g. valves, flange accessible for leak detection and maintenance.
- routing of offgases to nearby heaters/incinerators/flares for destruction as appropriate.
- steam injection on high level flares to maximise combustion efficiency and minimise slippage of non-combusted/partially combusted VOCs.

Table II.13 VOC Controls in Refinery Process Units (Installed and Retrofitted)

Emission Source	Refinery Process Units and Equipment	
Control Technology	Leak Detection and Repair Programmes	Collection of atmospheric VOCs and relief valves to flare/incineration system
Efficiency	50 - 90%	up to 99.5% destruction efficiency in incineration
Investment Costs	Moderate	1.3 M EUR for 5 Mt/y refinery(2)
Operating Costs	0.1-0.15 M EUR for 300 000 BPSD Refinery(1) 0.06 M EUR for 5 Mt/y refinery(2) 0.04 -0.08 M EUR/y for a 10 000 ppm programme to 0.8 M EUR/y for a 100-500 ppm programme(3)	3.0 M EUR(2)
Other Impacts	Costs of repair not included in above	Increase in CO_2 emissions due to combustion

Source (1) Industry Propriety Information
(2) UN-ECE EC AIR/WG6/1998/5
(3) Hydrocarbon Processing, September 1996, p 121

II.5.3. WASTE WATER COLLECTION AND TREATMENT SYSTEMS

Overview

Oily waters are produced at various stages of refinery processes (see also **Section III**) and these oily waters can contribute to VOC emissions to the atmosphere. The oily waters are typically transferred to gravity type water/oil separators for recovery of the oil. Some of the oil floats on the surface of the separator for recovery and a portion of this will evaporate. Evaporation is exacerbated where temperatures are elevated and there is an increased level of turbulence. There may also be drains, sewer boxes, intermediate sumps or open systems en route to the main separators where evaporation will also take place.

Minimise Contaminants

The first level of control is to ensure that these VOC emissions are minimised by preventing oil from contaminating refinery storm water drainage and cooling water systems and reducing, as far as possible, the contamination of process water. Reducing oil contamination is the most cost-effective way of reducing air emissions from wastewater collection and treatment systems. A high standard of maintenance and good housekeeping through policies, procedures and training should be adopted upstream. Operations to consider would include ensuring desalter effluent rundown temperature and oil content are minimised, separators are regularly, if not continuously skimmed, waste water strippers are operated optimally, high quality slops (low water content) are not introduced into the waste water treatment system. Drainage of tanks using automatic or semi-automatic draining devices with oil/water interface detection and oil recovery where possible can also be adopted particularly on light products and crudes.

Seals and Covers

The next level of control is to install water seals (traps) on sewers and drains and gas tight covers on junction boxes in the system. The use of covers on oil/water separators with good oil removal facilities will prevent or reduce evaporation of liquid hydrocarbons from exposed surfaces. Alternatively, incineration of the vapours coming from the API could be achieved from a covered API separator. The system would require piping, extraction fan costs are given in **Table II.14**.

Table II.14 VOC Controls in Oily Water Operations (Installed and Retrofitted)

Emission Source	Oily water sewers/sumps/separations and drainage operations			
Control Technology	Automatic drainage facilities	Fixed/floating covers on APIs/sump	Incineration	'dry' oil collection systems
Efficiency	80%	80-90%	98%	90%
Investment Costs	0.002 - 0.03 M EUR/tank (1)	0.001 M EUR/m^2 (1)	1M EUR(1)	?
Operating Costs	Small	Moderate	0.1 M EUR/y(1)	?
Other Impacts Comments	May not be suitable for all tank stocks	Limitation on access to APIs. Fixed covers may require purging systems	Assumes API is covered	?

Source (1) Industry Propriety Information

II.5.4. STORAGE

Overview

Crude oil, other feedstocks, and petroleum products are stored in various types of tanks and supplied to and shipped from refineries by:

- seagoing vessels
- barges
- rail tank cars
- tank trucks
- pipelines

The main sources of VOC emissions from storage are:

- breathing losses (in tanks)
- working losses (displacement and withdrawal in tanks)
- vapours released during water draining
- roof landings in floating roof tanks

Tanks for the storage of hydrocarbon liquids produce emissions to atmosphere either from vent ports, imperfect-sealing arrangements or from tank fittings. Evaporative losses from refinery tankage can represent a significant proportion of the total loss (as much as 30% at some locations depending on the seals and the control of other sources).

There are 4 categories of storage in general use:

- Fixed roof tanks
- External floating roof tanks (EFRTs)
- Internal floating roof tanks (IFRTs)
- Pressure Vessels

Appropriate Storage

Primary control for emissions from storage is therefore to ensure the liquids and gases stored are in appropriate vessels. Releases to air caused by evaporation/filling losses from crude oil, intermediates and product storage should be minimised by use of appropriate tanks or vessels based upon the true vapour pressure of the stored material, according to **Table II.15**.

Table II.15 Appropriate Storage

True vapour pressure at storage temperature	Type of tank or vessel
Up to 14 kPa (2 psia)	Fixed roof tank vented to atmosphere
Above 14 kPa (2 psia), and up to 91 kPa (13 psia)	External floating roof tank with primary and secondary rim seals, or fixed roof tank with internal floating deck fitted with primary seal, or fixed roof tank with vapour recovery system
Above 91 kPa (13 psia)	Pressure vessel

Emissions from hydrocarbon liquids in storage occur because of evaporative loss of the liquid during its storage and as a result of changes in the liquid level. The emission sources vary with tank design, as does the relative contribution of each type of emission source.

Fixed roof tank emissions are a result of standing emissions and working emissions. Standing loss is the expulsion of vapour from a tank through vapour expansion and contraction, the result of changes in temperature and barometric pressure. This loss occurs without any liquid level change in the tank. Working loss is the combined loss from filling and emptying. As the liquid level increases, the pressure inside the tank exceeds the relief pressure and vapours are expelled from the tank. Evaporative loss during emptying occurs when air drawn into the tank during liquid removal becomes saturated with organic vapour. As more hydrocarbons are evaporated to re-establish the air/hydrocarbon equilibrium, and expands, thus exceeding the vapour space capacity. Generally, for fixed roof tanks, working emissions are more important than standing emissions.

External floating roof tank emissions comprise withdrawal and standing emissions. Withdrawal emissions occur when the liquid level and hence the floating roof, is lowered leaving liquid remaining on the inner sides of the tank wall which subsequently evaporates into the atmosphere. Standing storage emissions from floating roof tanks include rim seal and roof-fitting emissions, which result from stock vapour pressure changes due to temperature, and pressure variations but more importantly wind effects. The influence of wind effects is not a factor on internal floating roof tanks. Standing emissions on external floating roof tanks are generally much more significant than withdrawal emissions.

External floating roof tanks are required for crudes or light products and generally result in much greater emissions than fixed roof tanks storing heavier stocks.

As with EFRT's, evaporative emissions from internal floating roof tanks (IFRT) primarily occur during standing storage, with an additional contribution from withdrawal emissions. In addition to the rim seal area and roof fitting penetrations, sources of standing loss from IFRTs include bolted seams in the floating roof.

Pressurised vessels such as bullets and spheres are often fitted with pressure relief valves, which vent to atmosphere or flare. VOC emissions can occur where these valves or by-pass block valves have internal leaks.

Reduction Technologies for Storage

Standing emissions from the floating roof tanks are the most important emissions to consider when determining storage tank emissions. All EFRT's are fitted with primary seals.

Fitting secondary roof rim seals is an accepted technology for emission reduction. Rim mounted seals (as opposed to shoe mounted seals) are favoured since the former offers emission control if the primary seal fails.

An acceptable alternative to an EFRT is to retrofit a fixed roof cover converting the EFRT to an internal floating roof (IFRT).

The costs of retrofits are given in **Table II.16** below. Costs are dependent on the tank diameter.

In many cases for an EFRT the emissions through fittings can exceed the rim seal losses especially on tanks with secondary seals. In terms of fitting losses, the major source is from the slotted stillwell (sample well or dipping well). Technologies to minimise emissions there include:

- installing wipers at the floating deck
- sleeves around the pipe, incorporating still well wipers
- floats with wipers inside the slotted pipe

Relief valves on pressurised storage should undergo periodic checks for internal leaks. This can be carried out using portable acoustic monitors or if venting to atmosphere with an accessible open end, tested with a hydrocarbon analyser as part of an LDAR programme.

Table II.16 VOC Controls in Storage (Installed and Retrofitted)

Emission Source	Refinery Storage		
Control Technology	Internal Floating Roofs in fixed roof tanks	Secondary/Double Seals on Floating Roof Tanks	Other Roof Fitting Emission Controls (roof legs, still wells) and options (tank paint)
Efficiency	90-95%	95%	up to 95% when together with secondary seals
Investment Costs M EUR	0.20 -> 0.40 for tanks(1) 20 - 60 metres diameter	0.05 - 0.10 for tanks(2) 20-50 metres diameter	0.006 for 50 metre tanks(1)
Operating Costs	Minor	Replacement every 10 years	Minor
Other Impacts Comments	Requires tank to be taken out of commission Reduces the net storage by 5-10%	Can reduce maximum storage capacity of tank	Not suitable for high sulphur crude oils due to pyrophoric scale possibility

References

(1) UN-ECE/IFARE, and Industry Propriety Information

(2) UN-ECE/IFARE and Industry Propriety Information (UN-ECE EC AIR/WG6/1998/5)

II.5.5. LOADING / UNLOADING

Overview

EC legislation requires that emissions be controlled from gasoline distribution systems (Stage 1). This mainly impacts loading operations at rail, road and shipping (barge traffic) operations where vapour recovery takes place. However, other products may need to have emission controls.

Vessels and barges

Displaced vapour containing air/gas from loading of volatile products (such as gasoline or products of similar vapour pressure) from vessels and barges should ideally be recycled or routed through a vapour recovery unit. When the product is loaded from a floating roof tank the vapours may be routed directly to a vapour recovery plant, incineration unit, or flare.

Rail tankers / road trucks

In addition to vapour recovery, for loading/unloading of rail tankers / road trucks there are several alternatives to minimise vapour emissions. These are:

- Bottom Loading:

  The loading/unloading pipe is flange-connected to a nozzle situated at the lowest point of the tank. A vent pipe on the tank is connected to a gas balancing line.
  The flange connection in the filling line has a special design ("dry connection") which enables it to be disconnected with minimum spillage/emissions.
  LPG and similar products are stored and transported in pressurised containers and handled in an essentially emission free manner.

- Vapour Balancing:

  Vapours expelled during loading operations may be returned to the loading tank if it is of the fixed roof type where it can be stored prior to vapour recovery or destruction. This system can be also used for vessels and barges.

Available Abatement Technologies

Among the abatement measures appropriate in refinery operations the following techniques may include:

- destruction of vented products in process heaters or special incinerators or flares.
- vapour recovery systems, being utilised for the reduction of hydrocarbon emissions from storage and loading facilities of gasoline and other highly volatile products. Such vapour recovery systems may consist of the following basic components :
  1. A gas collecting or balancing system.
  2. A recovery system utilising such measures as adsorption, absorption and condensation and/or incineration of the remaining VOC.

Hydrocarbon Vapour Recovery Technology

Hydrocarbon vapours are vented from gasoline or crude oil tank transfer operations. The hydrocarbons are usually vented as a mixture with air or inert gas.

Vapour recovery involves two processes:

- Separation of the hydrocarbons from the air
- Re-condensation of the separated hydrocarbons to the liquid state

Separation

There are four processes that may be used to separate hydrocarbon vapours from the permanent gases:

- Pressure swing adsorption on activated carbon
- Absorption by lean oil washing
- Selective membrane separation
- Condensation by cooling or compression (this is a special case because separation and re-condensation are both achieved in a single process)

Re-condensation

There are three processes, which are primarily used in Europe to achieve re-condensation of the separated hydrocarbon vapours:

- Re-absorption into the gasoline or crude oil

- Condensation
- Compression

Commercially Available Vapour Recovery Systems

For recovery of gasoline vapours there are four types of systems in use

- Pressure swing adsorption onto activated carbon, with re-absorption of the recovered vapours into a stream of gasoline
- Lean oil absorption using kerosene at –30°C, followed by splitting (kerosene is heated to drive off the hydrocarbon vapours) and re-absorption of the recovered vapours into a stream of gasoline
- Condensation and refrigeration
- Membrane separation by enrichment

For recovery of crude oil vapours, carbon adsorption is not considered suitable because of the possibility of contamination. Commercially available systems include:

- Lean oil absorption using kerosene at –30°C, followed by splitting and re-absorption of the recovered vapours into a stream of crude oil
- Compression, followed by re-absorption into the crude oil at 10 bar pressure
- Compression, followed by re-condensation by cooling to approximately –40°C.

Capital expenditure (CAPEX) of recovery and destruction technologies versus loading rate are given in **Figure II.2**. Capex versus capacity is given in **Figure II.3**.

Some data on the technologies in loading discussed are presented in **Table II.17**

Figure II.2 CAPEX Recovery and Destruction Technologies versus Loading Rate

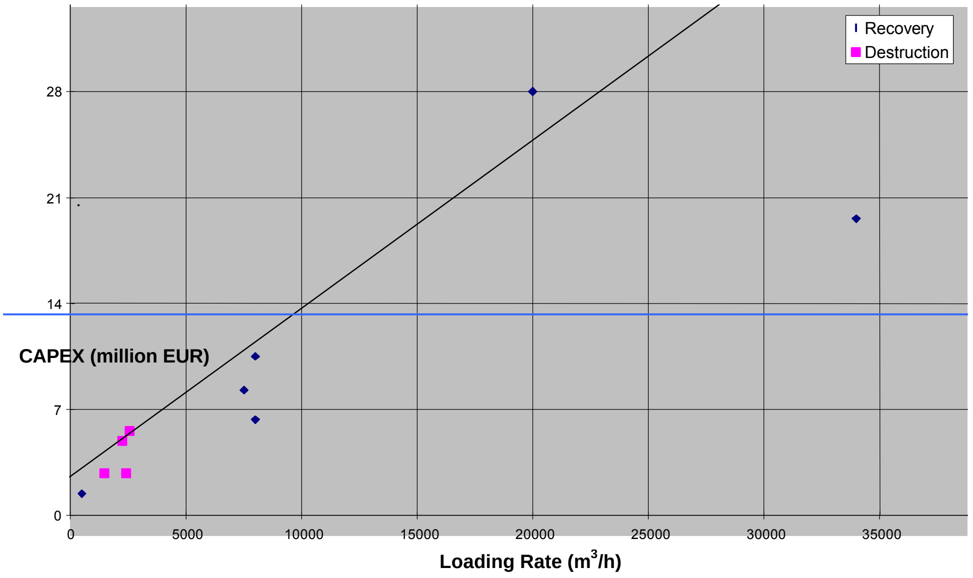


Figure II.3 Capital Expenditure (CAPEX) versus Capacity

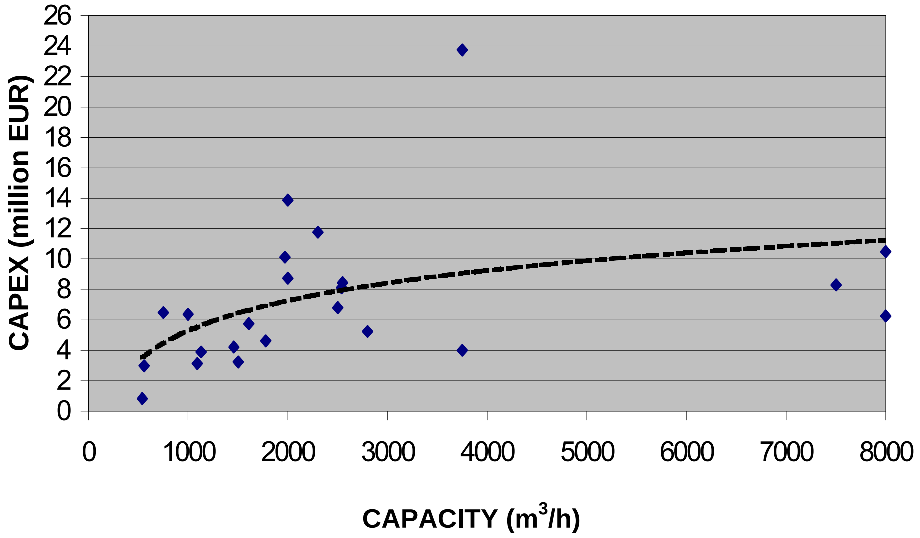


Table II.17 VOC Controls in Loading Operations (Installed and Retrofitted)

Emission Source	Loading Operations (slurry, road, rail and internal refinery movements)	
Control Technology	Improved Vapour Balancing and Operations	Vapour Collection followed by Recovery/ Destruction
Efficiency	up to 80%	up to 99.2%
Investment Costs M EUR	0.08 (1)	2 –25 (1) and (2) 3.2-16 M EUR for Marine loading 0.1-0.22 M EUR /ship for conversion (3)
Operating Costs M EUR	Low	0.02-1 (1) and (2) 0.22-1.1 (3)
Other Impacts/ comments	Not all vapours can be collected. May impact loading rates and operational flexibility Need to prevent explosive mixtures	Retrofit costs very site specific

References

(1) Industry Propriety Information

(2) UN-ECE/IFARE

(3) CONCAWE Review. Volume 7, No. 2, October 1998. Cost Effectiveness of Marine Vapour Emissions Control

II.5.6. MONITORING OF VOCs

For both technical and practical reasons, it is normally not feasible to conduct direct measurement of emissions from diffuse sources. The optimum approach to avoid disproportionate emissions from such sources is a concerted programme of preventative maintenance and leak detection and repair programmes combined with close plant surveillance by the plant operators concentrating on the point sources.

Technologies

There are a number of spatial gas detection systems available to assist in monitoring emissions. Expensive systems such as DIAL (Differential Absorption Lidar) can be used on an infrequent basis to identify hot spots of VOC concentrations and therefore areas of large leaks in refinery facilities. Less complex systems such as LPM (Long Path Monitors) or point source detectors may be used for continuous monitoring of some areas but will not provide information on actual sources of emissions.

Latest developments in leak detection and repair include the development of a 'SMART LDAR' system.[3] This device is able to detect (using laser technology) hydrocarbon fugitive emissions to real time video image of the equipment under surveillance. This technology is under development and still needs resolution of a number of technical issues before it is ready for use as routine tool. Nevertheless these developments over conventional LDAR programmes are likely to mature in the near term and progress should be monitored to see when they could be accepted as BAT.

Metering systems provide a means of monitoring and quantifying VOC emissions from flares. Ultrasonic time-of-flight devices offer the best accuracy and can provide data on gas properties through molecular weight output to assist in source control. Surveys of relief valves using portable acoustic monitors, to identify valves leaking to the flare system, will aid flare reduction and therefore directionally any VOC emissions from flares.

II.5.7. SAFETY ISSUES

Considerable care needs to be taken in both the design and operation of vapour balancing and vapour recovery systems. Connecting a number of essentially uncontrolled vapour sources can mean that the gas composition in the vapour space can potentially move in and out of the explosive range. Measures are therefore required to ensure that fire/explosion in one part of the system can not spread throughout the system.

II.6. PARTICULATE MATTER (PM)

Two main sources of particulates exist in refineries:

1. Process heaters and boilers (burning oil)
2. Fluid Catalytic Cracking Units (FCCU) and more specifically the catalyst regenerators of such units

Emissions can vary greatly depending, for process heaters and boilers on fuel quality and the operation, but also on the design of burners and furnaces. For catalyst regenerators it depends on the type of dust catching equipment, equipment maintenance and catalyst properties.

Measurement of particulates is possible directly or, more commonly by using opacity.

II.6.1. PARTICULATE EMISSIONS FROM OIL FIRED EQUIPMENT

The particulate matter in flue gases can take any of the following four forms

- soot, the particle size is below 1 µm – visible smoke from a stack is caused by all particles but mainly 0.5 to 5 µm
- cenospheres : they originate from the liquid phase residues of combustion of heavy oil droplets, at relatively low temperature (< 700 °C), the size is equal to or larger than that of the original oil droplets
- coke particles, formed through liquid phase cracking in combustion at high temperatures (> 700 °C). The particle size is generally from 1 to 10 µm.
- fine particles (< 0,01 µm): their contribution to the total mass emission is negligible.

Under normal conditions, the solids in the flue gases of a furnace or boiler consist mainly of coke particles with some cenospheres, depending on the conditions of firing. The particulate emission of oil fired equipment may vary considerably. It depends on a number of more or less independent parameters such as: fuel type, burner design, oxygen concentration at the outlet of the radiant section, the flue gas outlet temperature of the radiant box, and the residence time of the fuel droplets. Globally the quantity of emission from oil firing is very small. For older furnaces liquid refinery fuel fired flue gas levels may range from 500 to 1000 mg/Nm^3. For new optimal burner design with steam atomisation this can be well below 200 mg/Nm^3. For boilers, all these figures are on average lower.

II.6.2. PARTICULATE EMISSIONS FROM FLUID CATALYTIC CRACKING UNITS

In a catalytic cracking unit a heavy oil fraction is brought into contact with a hot stream of finely dispersed catalyst particles (size 5 to 125 μm) in a reactor.

During the cracking reaction, coke is deposited on the catalyst, which is therefore passed to a regenerator where the coke is burned off before recycling the catalyst to the reactor. Since considerable entrainment of catalyst with the combustion gases occurs, the gases are passed through cyclones before disposal to the regenerator stack.

The particle size distribution shows that almost up to 90% by weight can be smaller than 10 μm. In practice, operating conditions may have a large effect on particulate emissions, and the control of particulate emission from FCCU has been practised for a long time in refineries.

Several regenerator types are installed in European refineries. The basic design includes two stage cyclones in the regenerator vessel, which prevent the bulk of the catalyst from escaping the system. However smaller catalyst particles, some of which are introduced with fresh catalyst and some created by attrition in the circulating system are not easily retained by the two stage cyclone system.

To improve control of emission of particles, different measures can be used in the operating parameters. Secondary emission control equipment can also be used but the most appropriate device will be very site specific. A number of possibilities for recovery of particles from regenerator flue gas are available. The most frequently encountered are:

- tertiary cyclones
- multi cyclones
- electrostatic precipitators
- wet flue gas scrubbers

Tertiary cyclones

This is the natural first choice of clean up device for particulates: these are conventional cyclones, fitted externally to the regenerator but operating on the same principle as the internal first and second cyclones.

They are high velocity devices and recovered catalyst is returned to a dust hopper.

Multi-cyclones

This alternative has been developed for the protection of flue gas power recovery, it is more effective for coarser particles and it has been designed to prevent essentially any particles greater than 10 microns from entering the turbine.

This is a system depending on centrifugal separation of particles at high speed, the gas stream being distributed over a number of parallel small cyclones. A fourth stage cyclone treats the small amount of gas carrying the catalyst particles separated in the multicyclones.

Electrostatic precipitator ESP

ESPs are of many types and configurations but all are derived from the same principles. The device creates an electric charge on the catalyst particles to move them out the main gas stream onto the electrode wall, allowing them to settle into a collection device. The ESP requires several compartments to achieve this and a large volume to ensure that gas velocities are low enough to give the particles time to migrate to the wall area. A system is used to mechanically shock or vibrate the collector plates, thereby dislodging the precipitated dust, which drops into hoppers.

Wet gas scrubbers

The system is an efficient particulate emission abatement tool. However it creates secondary problems of aqueous slurry waste disposal and increased refinery energy consumption.

Table II.18 Fluid Catalytic Cracking Emission Control for Particulates

Example: Capacity of process: 1.5 Mt/y (FCC) (30 000 bpd) coke 75 000 t/y
Volume of gas: 10^9 m^3/y
Pollutant: initial concentration 4 000 mg/m^3 (S in feed approx. 2.5%)
(These values may vary depending on feed and process)

Name of technique	3rd cyclone	Multi cyclones	Electrostatic precipitator (ESP)	Wet gas scrubber	Catalyst selection
Efficiency	30-40 %	50 to 70%	90-95%	Up to 95%	Up to 85%
Typical downstream effluent	40-250 mg/m^3	60-250 mg/m^3	< 50 mg/m^3	< 50 mg/m^3	Down to 300 mg/m^3
Investment expenses	1-2.5 M EUR	1-2 M EUR	4-6 M EUR	4-6 M EUR	none
Operating expenses	0.7 M EUR/y	0.1 M EUR/y	0.25-0.5 M EUR/y	2-5 M EUR/y	Negl.
Other impacts	Fine catalyst disposal 300-400 ton/y/unit (disposal cost 120/300 EUR/ton – incl. Transportation)	Possible energy consumption reduction (power recovery)	Increased energy (electricity) consumption. Fine catalyst disposal	Waste water (Na_2SO_4) Reduced SO_2 emission. Increased energy consumption	May increase coke yield

Source: Industry

Note: Operating costs include only cash direct operating expenses i.e. do not include depreciation of investment, nor financial charges. Investment costs refer to new plant installation (see section for retrofitting existing plants)

II.6.3. PARTICULATE EMISSIONS FROM COKING PLANTS

Description

Coking as described here is a severe thermal cracking process that maximises the severity to the extent that coke is formed while production of the more profitable light products is maximised.

The coke plant appears in this framework as a thermal conversion unit that:

- processes heavy residuals
- further improves the yields in terms of light products.

The process can be described as follows:

Heavy fractions, such as residues from vacuum distillation or thermal cracking units, are fed to a fractionator, the bottoms from which are fed to a process heater that raises the temperature to around 500 °C. The heated oil is then fed to a coke drum where it "soaks" for approximately 12 hours (another 12 hours are required to cool the drum and recover coke) producing "green" coke. The oil vapours from the coke drum are separated in a fractionating column. The green coke is transferred to the calcining unit where, in the case of production of special grade cokes (anode, needle), the residual volatile material is removed, otherwise green coke is disposed of for direct use as fuel for power generation etc. The unburnt gases from the calciner are burned in an incinerator, then passed through a waste heat boiler before being released to the atmosphere via a dust collection system.

Emissions

Emissions of a coke plant are, apart from furnace flue gas; coke fines (particulates) from handling of coke and from the calciner.

Control of emissions

Coke fines emissions are controlled with adequate systems to prevent emissions at the various stages of the process.

The best available techniques to reduce particulate emissions from the calciner associated with a coke plant are similar to those already presented for limiting particulate emissions from the FCC (see **Table II.18** above). In addition bag filters can be used at a cost of about 5 M EUR.

For coke handling, particularly when green coke is used as fuel, the best available technology relevant to closed systems to minimise coke fines release, has an investment cost of about 30 M EUR for a typical coking unit with a capacity of 1.5 Mt/year.

II.7. ENERGY AND FUEL MANAGEMENT

II.7.1. FUEL MANAGEMENT

Fuel management has the primary objective of supplying the refinery effectively with the necessary heat for crude oil processing and utilities (steam/power) generation taking into account the available fuel slate. This involves optimising refinery operating costs and, in this "BAT" context, to effectively reduce the impact on the environment.

Refinery fuel management must observe several limiting factors and constraints that are specific for each single refinery.

- refinery configuration and crudes processed (especially their sulphur contents),
- complexity with respect to number of units and the degree of process and energy integration of the various units.
- age of the various units and technology restrictions,
- fuel requirements in relation to quantity and quality of produced fuels,
- safety and environmental restrictions imposed on individual units or the refinery complex,
- operational flexibility or limitations within the refinery system,
- climatic and/or local conditions

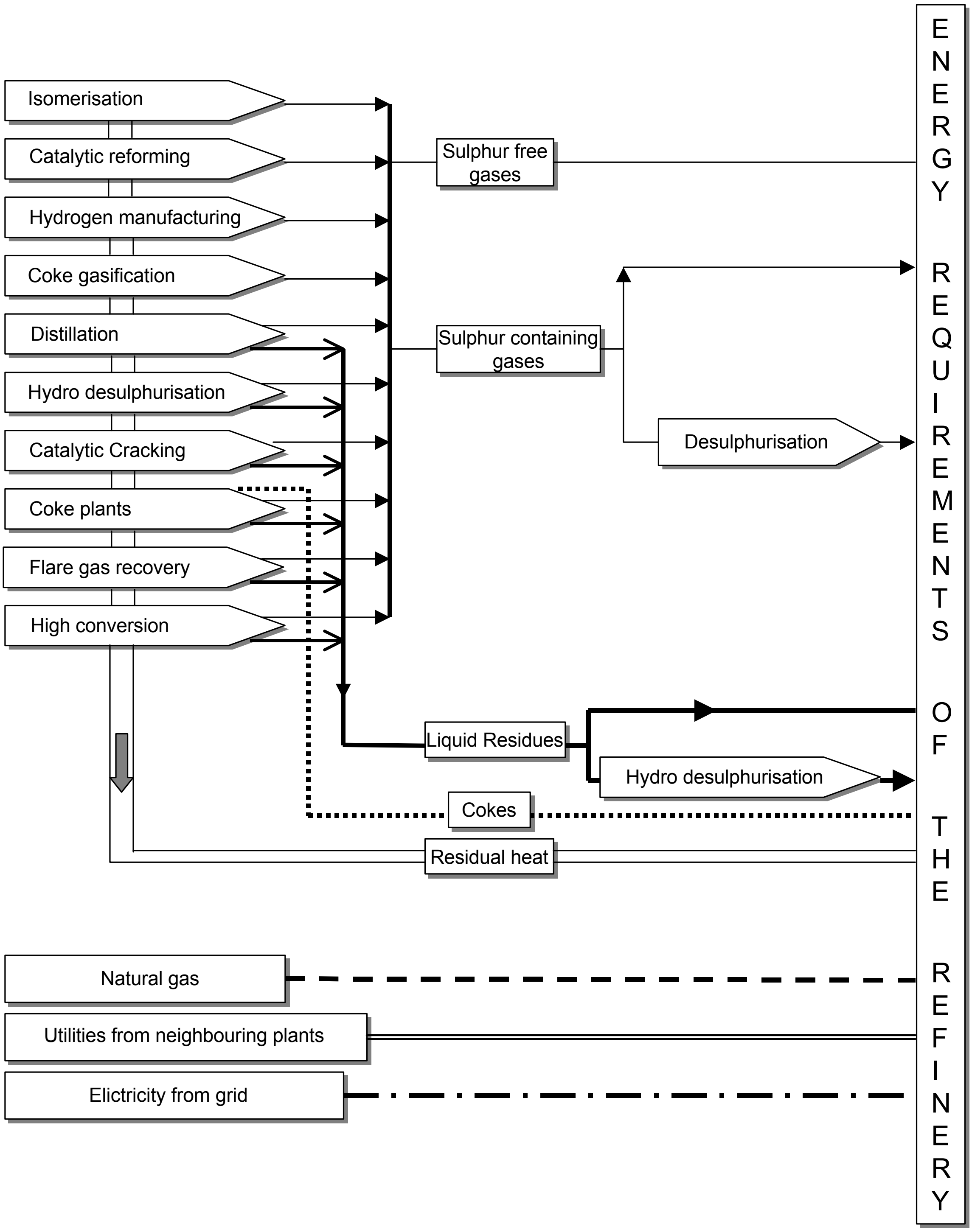
A schematic diagram of a refinery fuel system is presented in **Figure II.4**.

II.7.2. REFINERY FUELS

In refineries either gaseous or liquid fuels are commonly used to supply the necessary energy and power requirements. The fuels are normally produced in the various refinery processes.

These fuels often consist of process streams that cannot be easily converted into marketable products i.e. refinery gases and heavy residual hydrocarbon streams. The refinery gases are by-products from the various processes. As the gases cannot normally be stored in a refinery these fuels have to be used immediately. Therefore these fuels supply the base load of the energy demand of the refinery. The liquid fuel streams normally provide the balance of the fuel required for refinery operation. In addition the coke deposits on Fluid Catalytic Cracking catalysts or coke from some types of coking operations provide other but very specific sources of refinery energy. Natural gas is sometimes imported into refineries as a balancing fuel or as feedstock for hydrogen production.

Figure II.4 Example of Energy Sources Produced/ Used in a Refinery (main possible flows)



II.7.3. REFINERY FUEL DEMAND

As refinery fuels are produced along with the refinery operation, fuel demand and production of a refinery are determined by more or less the same factors e.g.:

- refinery capacity,
- refinery complexity,
- energy efficiency,
- capacity and capacity utilisation of process units,
- product slate (range),
- product quality,
- on site generation of electricity versus purchasing from outside,
- storage and loading facilities,
- existence of chemical manufacturing plants on the refinery site,
- exchange of utilities with other industries,

The refinery fuel demand is often expressed as a % wt on crude oil intake and it may vary between 2 - 3 % for hydroskimming refineries to 4 - 7 % for the complex, high conversion refineries. Rational use of refinery fuels as a prime objective has resulted in a distinct reduction of the fuel demand percentage during the past 20 years.

II.7.4. SUPPLY / DEMAND

An important objective in fuel management is, therefore, to match variable consumption with variable production at an optimised cost level while at the same time meeting environmental and safety constraints.

The installation of gas turbines may enable efficient combined production of steam and electricity. Part of the refinery steam demand can be produced in waste heat boilers. Production of low pressure steam from flue gases is also practised to recover maximum energy from these streams.

Alterations in supply (crude/feedstock) result in changes of fuel production quantity as well as of fuel quality. Variations of the sulphur content may require alterations in the refinery fuel composition.

II.7.5. ENVIRONMENTAL CONSIDERATIONS

Elements for environmental considerations of the refinery fuel system are:

- fuel consumption, efficient energy use and CO_2 emission
- fuel sulphur content and SO_2 emissions
- nitrogen oxide formation in the combustion process
- particle formation from ash and incomplete burnout

Fuel saving, especially of residual fuel, by increasing energy efficiency, has a beneficial influence on all four parameters. Please also see the various sections where each of the pollutants is discussed.

II.7.6. REFINERY FUEL GAS

Sources (Figure II.4)

Refinery fuel gases are produced in almost all hydrocarbon processing installations. From an environmental point of view they can be classified as sulphur-free and sulphur-containing gases.

Sources of sulphur-free gases

The sulphur-free gases originate from the following sources:

- catalytic reforming plants,
- hydrogen manufacturing plants,
- gasification of coke in some coking operations,
- isomerisation plants.

As a consequence of the use of sulphur sensitive catalysts in catalytic reforming and isomerisation, these processes require virtually sulphur-free feedstocks (e.g. desulphurised light hydrocarbon streams and naphtha). As a result the gas streams from these units are also virtually sulphur-free. The gases produced in hydrogen manufacturing plants and from gasification units are normally also sulphur-free.

Sources of sulphur containing gases

Most of the other gases produced in the refinery contain hydrogen sulphide (H_2S) and often small quantities of mercaptans i.e. from:

- crude distillation,
- hydrotreating / hydrodesulphurisation,
- catalytic cracking,
- thermal cracking / coking / visbreaking,
- residue conversion,
- flare gas recovery,
- gasification of coke from some coking operations.

Fuel gas composition

Refinery fuel gas predominantly comprises hydrogen, methane, C_2-C_5 hydrocarbons (saturated/unsaturated), hydrogen sulphide, mercaptans, sometimes nitrogen in varying quantities and, in the case of steam-reformer type hydrogen units, also carbon monoxide. The sulphur content of the gas streams contributing to the fuel gas can be reduced to the required level by sophisticated sour gas treatment. Generally the low heat value gas from the steam-reformer, which contains carbon monoxide and hydrogen is burned in the furnace of that unit and is not distributed to the net.

Refinery fuel gas system

A refinery fuel gas system may consist of more than one grid, each of which has its own operational and safety requirements. Balancing fuel gas production, fuel gas demand and fuel gas quality with the total heat demand of the refinery and the required emission control can only be achieved by extensive control mechanisms.

II.7.7. LIQUID REFINERY FUEL

Sources of liquid fuels

Liquid refinery fuel streams originate from various processes such as crude fractionation, high vacuum distillation, thermal cracking, catalytic cracking and from hydro conversion of residues. Except for the latter, the sulphur content of these residues can only be controlled by feedstock choice. Lubricating oil production can also supply fuel oil components.

In general, the liquid fuel may comprise one or more of the following components : atmospheric and vacuum residues, thermally or catalytically cracked residues, heavy cat cracked cycle oil and hydrocracked residue. Sulphur contents of liquid refinery fuel components are :

- Atmospheric residue
  - From North Sea 0.6 - 1.1 %
  - From Middle East 2.3 - 4.4 %
- Vacuum residue
  - From North Sea 1.1 - 1.8 %
  - From Middle East 3.6 - 6.1 %
- Cracked residue
  - From Middle East 3.5 - 6.5 %

While the sulphur content of refinery fuel gas can be reduced to very low levels by commonly available techniques there are no such means for heavy liquid fuels. The only way to limit the sulphur content of residual fuels is by selection of crude oil sources. Residue desulphurisation has not proved viable for SO_2 emission control inside or outside refineries.

II.7.8. OPTIMISATION AND COST EFFECTIVENESS OF FUEL MANAGEMENT

For SO_2, the total emissions of the refinery are directly linked to the SO_2 concentration in all the flue gases in the refinery respective to the sulphur content of the refinery fuels plus the SO_2 contained in FCC and Sulphur Recovery Unit off gas. The extent of controlling SO_2 emissions by fuel management is governed by the officially set limit that is derived from the politically defined abatement strategy. To comply with this limit the refinery management has to decide whether to use adequate low sulphur fuels at higher cost or whether to invest selectively in equipment for SO_2 emission reduction. Refineries in Europe have done both. [2]
Refineries have been increasing the use of low sulphur crude oils or processes for removal of sulphur from streams used to blend the finished products. This sulphur is normally recovered as elemental sulphur.

Comparative data for 1992 and 1995 already show the impact of these measures. Sulphur in oil combustion products declined from 51% of the total intake in 1992, to 40% in 1995. There was a corresponding improvement in sulphur recovery in refineries, which increased from 27% of the sulphur input in 1992, to 36% in 1995.

Fuels other than conventional oil and gas contributed 7% of total refinery fuel, an increase of 3% on 1992. The 1995 refinery fuel SO_2 bubble, based on total flue gas volumes from all fuels, was the same as in 1992. Since the energy requirement in 1995 was 11% higher than in 1992, this means that the SO_2 emission per unit of energy consumed decreased substantially.

For NO_x emission reduction measures, a different concept is required to be cost-effective. The nitrogen content of fuels is only one parameter influencing NO_x emissions and cannot be controlled by any economically feasible refinery processes. Higher NO_x concentrations in some furnaces can be compensated by investment in NO_x reduction equipment in other furnaces where the cost of reduction is lower and the abatement efficiency is higher. It must be emphasised that NO_x reduction may increase the overall energy consumption and also other pollutant emissions e.g. particulates.

The design of burners, furnaces and boilers has an impact on NO_x and particulate emissions. This should be taken into account when new equipment is installed in refineries. The specification of the equipment should fully consider fuel efficiency and pollutant emissions reduction.

CO_2 emissions vary directly with:

- the total energy consumption of the refinery
- the relative share of light to heavy products in the refinery fuel mix. As light hydrocarbons contain a relatively higher quantity of hydrogen versus carbon, they produce less CO_2 emissions than heavy products.

CO_2 reduction in refineries is not a goal as such, but a result of the normal optimisation efforts by fuel balancing and energy conservation.

II.8. CATALYST MANAGEMENT

II.8.1. CATALYST DEFINITION

Solid catalysts are employed in the following processes :

- isomerisation,
- catalytic reforming,
- hydrodesulphurisation,
- hydrocracking,
- residue conversion / desulphurisation,
- sulphur recovery,

and also in FCC units which have already been discussed.

II.8.2. SOLID CATALYSTS IN FIXED-BED AND FLUID-BED APPLICATIONS, EXCLUDING CAT CRACKING

In general, catalysts deactivate during use as a result of carbonaceous deposits (coke) or by contamination with heavy metals, which are present in residual hydrocarbon streams. In order to enable effective utilisation most catalysts are regenerated at regular intervals to restore their activity. Usually the regeneration process involves a coke removal step by controlled burn off with oxygen/air. When sulphur compounds (metal sulphides) are present in the catalyst, they are normally subjected to off-site regeneration by a specialised company.

Regeneration intervals for fixed bed processes may vary from 6 months to 4 years. An average cycle length of 2 years can be assumed.

Isomerisation and cat reforming catalysts usually employ noble metals for processing virtually sulphur free feedstocks. Normally, the sulphur content of the used catalysts is well below 0.1 % wt and, at maximum, the contribution of these catalysts to sulphur dioxide production is less than 100 kg SO_2 per regeneration and therefore can be neglected.

Hydro-desulphurisation and hydrocracking catalyst may contain up to 10 % sulphur as metal sulphides, which form the active de-sulphurisation/ hydrogenation component on these catalysts. A large unit in this type of service may contain 150 tons of catalyst. During in-situ regeneration approximately 30 tons of SO_2 would be released into the atmosphere. Sometimes, odour problems are encountered during in situ regeneration. Therefore catalyst regeneration is normally performed off site by specialised catalyst manufacturers/ reclaimers.

As a consequence of the presence of heavy metals in the feedstocks that are normally processed, catalysts used in residue conversion and desulphurisation processes accumulate these heavy metals up to a high percentage during their process cycle. An in-situ regeneration burn-off of these types of catalysts is therefore not a suitable procedure for restoring catalyst activity. Normally these catalysts will be used on a non-regenerative basis. They may serve as raw materials for the recovery of heavy metals (Nickel or Vanadium).

Further information on the management, treatment and disposal of catalysts is given in **Section IV** – Waste.

II.9. NON ROUTINE CONDITIONS

These operations relate to two main events. Firstly the infrequent or **unplanned** shutdown or upset and the **planned** ‘turnarounds’ or shutdowns of refinery plant and equipment for maintenance or inspection. Typical planned shutdowns occur every 3 to 5 years, although statutory inspections for selected pieces of equipment e.g. boilers may be as frequent as every year. Also processes may have to shut down to change catalyst.

As all these operations involve the controlled release of hydrocarbons from plant and equipment, there is the potential release of VOCs, contaminated water and solid materials (e.g. sludges and catalysts). As such, refineries are designed and operated to prevent unnecessary emissions during these periods. Release of VOCs to atmosphere can often be the major issue during non-routine operations.

II.9.1. UNPLANNED EVENTS

These often involve the need to dispose of large quantities of VOC materials due to overpressure effects during upset conditions. Standard technology is to route most hydrocarbon service relief to the refinery flare system, where the gases can be combusted and disposed of in either elevated or ground flares. Best available technology includes the containment of these relief hydrocarbon streams either within the process, or their transfer to another part of the process so that relieving gases are minimised. Flares should be designed to cope with the calculated combustion needs for upsets and should have steam injection or other combustion improving technologies at the combustion point. Liquid releases (which are often very small) are either routed back to the process or to liquid collection systems. Any solids released should be contained.

II.9.2. PLANNED NON-ROUTINE OPERATIONS

Operational procedures and plant/equipment design are major factors in avoiding unnecessary emissions during planned outages. Process units should be closed down progressively with gases routed to refinery fuel gas or flare as a last resort and liquid hydrocarbons collected at low points and then routed into hard piped collection systems (dry oil systems). Oil stocks in storage tanks should be eliminated or minimised , e.g. pumping to an adjacent tank or treatment of oily sludges to remove oil, before opening to atmosphere. All oil contaminated from steaming out and gas-freeing operations should be collected and released in a controlled manner to the effluent treatment plant to avoid upsets which could adversely affect effluent quality. These operations may involve the use of temporary pipework and fittings to collect liquid washing and solid debris.

Offsite regeneration of catalysts will prevent the release of combustion products e.g. SO_2, CO_2 within the refinery area and avoid the possible need for off-gas treatment facilities that are available at off-site regeneration facilities.

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APPENDIX II

Table A II.1 Contribution to Total Emissions of the CORINAIR 90 Inventories (28 countries)

Source-activity	**Contribution to total emissions [%] of W. Europe**					
	SO_2	**NO_x**	**NM VOC**	**CH_4**	**CO**	**CO_2**
Process Furnaces	1.4	0.5	0.2	0	0.1	1.0
Petroleum Processes	0.5	0.1	0.7	0	0	0.2
Fluid Catalytic Cracking	0.4	0.1	0	-	0	0.1
Sulphur Recovery Units	0.3	-	0	-	0	-
Storage and Handling of Products in Refinery	-	-	0.4	-	-	-
Flaring in Petroleum Refineries	0.1	0.1	0	-	0	0

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)
- = no emissions are reported

Table A II.2 A Split of Total Refinery Emissions as an Example for SO_2 and NO_x Emissions (CORINAIR W-Europe):

Percentage SO_2 of total SO_2 emissions from refineries:	
- Process heaters and boilers	69 %
- FCC units (CO boilers)	7 %
- sulphur recovery unit	10 %
- flares	9 %
- other sources (e.g. gas turbines, stationary engines)	5 %

Percentage NO_x of total NO_x emissions from refineries	
- process heaters and boilers	63 %
- FCC units (CO boilers)	16 %
- engines (for pumps etc.)	11 %
- gas turbines and combined cycle systems	10 %

best available techniques to reduce emissions from refineries - water

Prepared for the CONCAWE Water Quality Management Group by its Special Task Force WQ/STF-28

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ABSTRACT

This report is one section of a report prepared by CONCAWE on the available technologies for environmental protection in the oil refining industry. It describes the available technologies for oil refinery waste water treatment and summarises actual data on facilities installed in refineries, their capital and operating costs, and design performance capabilities. Information is given on the quantities of effluents and sludges generated by oil refineries in Western Europe, the methods used to treat these effluents and sludges, and the costs of constructing and operating such treatment processes. It is intended to be part of the input for the development of BAT Reference Documents (BATREF) required under the Integrated Pollution Prevention & Control (IPPC) Directive.

KEYWORDS

cost, effluents, oil, refinery, sludges, treatment, waste, waste water

NOTE
Considerable efforts have been made to assure the accuracy and reliability of the information contained in this publication. However, neither CONCAWE nor any company participating in CONCAWE can accept liability for any loss, damage or injury whatsoever resulting from the use of this information.

This report does not necessarily represent the views of any company participating in CONCAWE.

CONTENTS

III.1. INTRODUCTION

This document is one section of a larger report prepared by CONCAWE on the available technologies for environmental protection in the oil refining industry. It is intended to be part of the input for the development of BAT Reference Documents (BATREF) required under the Integrated Pollution Prevention & Control (IPPC) Directive. [1]

The report summarises actual data on facilities installed in refineries, their capital and operating costs, and design performance capability. CONCAWE established Special Task Force WQ/STF-28 to study this subject and this report details their findings.

Since environmental controls are normally costly, and costs have ultimately to be borne by the consumer in terms of increased prices, it is clearly necessary to establish controls on the basis of sound science, risk assessment and cost/benefit and environmental need considerations. This CONCAWE report considers the full range of effluent water quality control techniques currently employed in European refineries, the cost of installing and operating them, and the performance they have been demonstrated to deliver. In other words, practical data are presented rather than that claimed by the designers/vendors of the equipment. The information was gathered by means of a questionnaire sent to all refineries during the latter part of 1996. The data are presented as a series of technical descriptions and tables of cost and performance.

An important point is that there is no such thing as a universal “BAT”. Oil refineries differ in their size, complexity, the types of processes they operate, and the types of crude they process. They are also situated in a range of climatic conditions and discharge into different types of receiving water. All these factors influence the volume and composition of effluent water to be treated and the level of performance required to protect the receiving environment.

It should be noted that since no new refineries have been built in recent years, the costs contained herein largely reflect retrofitting rather than "grass-roots" installations. Retrofitting is inevitably more expensive than installation at the time of original construction, since it may be influenced to a significant extent by the need to clear plot space, tie into existing facilities and build in areas that may already be congested with other operating equipment. The capital costs presented are therefore higher than would be indicated by equipment vendor's data. It is important that costs used in assessing the cost/benefit of any future BAT discussions reflect actual installed costs and not purchase prices. It must also be recognised that no two sites are the same, and the cost of installing particular facilities on one site may be very different from that for the same facilities on a different site - particularly if it is located in a different country.

Information was also requested on operating costs. The costs obtained mainly referred to those for consumables, *ie* chemicals and energy. Manpower costs were less easy to assess as in most cases, the individual effluent treatment plants considered were part of a much larger system and it was difficult to apportion the manpower between the various units. Some approximate manning levels were obtained but no attempt was made to convert these into costs as costs of manpower vary markedly across the different Member States of the EU. The choice of whether to increase automation at the expense of manpower may well therefore vary from country to country.

It is also important to consider the full implications of control measures employed. In particular, account must be taken of the generation of waste and cost and environmental impact of its disposal. The use of energy for treatment is also an important factor to be borne in mind.

By its nature, although the definition of BAT includes techniques as well as technology, it tends to concentrate on 'end of pipe' treatment. However, the use of appropriate techniques upstream to reduce either or both of the quantity of waste (including water) streams and the concentration of pollutants in them, can have significant effects in reducing the final emissions of pollutants. The techniques available which come under the general title of 'waste minimisation' are wide-ranging in nature and mainly fall outside the remit of this report. Some measures which come into this category and may be used in oil refineries are described in a CONCAWE Field Guide[2] and **Section IV** of this report.

The effluent treatment process is a major source of wastes in oil refineries as it generates sludges. The management of these is considered in this section of the report. Other wastes are not considered here but in **Section IV** of the combined report. Cooling water facilities are the subject of a separate "horizontal" BREF and are not considered in any detail in this report. Water re-use is a consideration associated with effluent systems, but is outside the scope of this document as it is very site specific.

III.2. WATER TREATMENT PROCESSES

III.2.1. GENERAL PRINCIPLES

Although there is no such thing as a standard refinery effluent treatment system, there are a number of general principles that are applied in most refineries. The main contaminants to be removed are oil, solid particles and dissolved substances, both organic and inorganic. These come from a wide range of sources and contain varying concentrations of contaminants.

III.2.1.1. Typical Contaminants

A guide to the range of contaminants present in some typical effluent streams is given in **Table III.1**. In a normal refinery, certain water streams which contain high quantities of sour gases (mainly hydrogen sulphide and ammonia) are stripped to lower the concentration of these gases before discharging them to the effluent treatment plant.

Table III.1 Representative Concentrations of Pollutants in Typical Refinery Effluents

	Oil	**H_2S (RSH)**	**NH_3 (NH_4^+)**	**Phenols**	**BOD COD TOC**	**CN- (CNS-)**	**TSS**
Distillation Units	XX	XX	XX	X	XX	-	XX
Hydrotreatment	XX	XX(X)	XX(X)	-	X(X)	-	-
Visbreaker	XX	XX	XX	XX	XX	X	X
Catalytic Cracking	XX	XXX	XXX	XX	XX	X	X
Hydrocracking	XX	XXX	XXX	-	X	-	-
Lube oil	XX	X	X	-	XX	-	-
Spent caustic	XX	XX	-	XXX	XXX	X	X
Ballast water	X	-	-	X	X	X	X
Utilities (Rain)	-(x)	-	-	-	X	-	-
Sanitary/Domestic	-	-	X	-	X	-	XX

Key: X =< 50 mg/l, XX =50 – 500 mg/l, XXX = > 500 mg/l

A typical refinery effluent plant consists of three main stages, primary, secondary and tertiary treatment. The purpose of the primary stage is to recover free oil and remove gross solids. In the secondary stage, dispersed oil and fine solids are removed, while in the tertiary stage, dissolved oil and other dissolved organic contaminants are removed. Each of these stages is described in the following sections.

All three stages generate sludges which have to be disposed of, and it is becoming increasingly common to pre-treat these sludges before disposal to recover oil and to remove water (see **Section III.3**).

III.2.1.2. Oil

Reference is frequently made in this report to “oil” in water. Although the meaning of the word oil is obvious to all, its measurement is less obvious and in strict terms has no real scientific meaning as it is impossible to analyse for oil as such. There are a number of methods which are in use to estimate the oil content of water. Of these, the most generally used are a family of tests in which the water sample is extracted with a non-water soluble solvent (e.g. freon). The extract is then often treated with an absorbent to remove polar compounds, and then analysed by infra-red spectroscopy (usually at three wavelengths) and the absorption compared with that of a reference standard of known concentration. The choice of a suitable solvent is currently under review. Carbon tetrachloride used to be used but was abandoned because of health concerns, and the use of freons is becoming more restricted because of environmental concerns.

It should be noted that even with this type of analysis, the results may vary depending on the actual solvent used, the solvent / sample ratio, the absorbent used, the wavelengths measured, and the composition of the reference standard, not to mention the type of oil in the sample being analysed. The result of this is that oil content should only be quoted with reference to the method used.

More importantly, emission standards must similarly be set against a defined analysis method. This may well mean that emission standards (and quoted effluent concentrations) will vary from place to place depending on the analytical method even where the standards are designed to achieve the same level of environmental protection. Similarly, if the method of analysis is changed, the emission standard should also be reassessed.

III.2.1.3. Monitoring

The monitoring of refinery effluents poses a number of special problems. Firstly, where free oil is present, it will be dispersed as droplets in the water phase, but in quiescent streams will tend to float to the top. It is therefore essential to only sample in areas of turbulent flow to ensure that a representative sample is obtained.

Secondly, when a sample is taken, some of the oil will float to the surface, and some will tend to be adsorbed onto the walls of the sample container. It is therefore essential to extract the whole sample and the sample container.

As is common with effluents from other industries, the effluent flow may vary and to take account of this, it is good practice to use a flow proportional sampling loop to collect samples.

III.2.2. FLOW BALANCING

In general, effluent treatment plants operate most effectively at a reasonably constant flow rate. However, in practice, both flow rates and pollutant load can fluctuate markedly due to factors such as process conditions, use of water for washing, ballast water treatment, rainfall, etc. To even out the flow and load, balancing capacity may be installed upstream of the primary treatment. This may be either in line or more usually installed as a side-stream to which flow can be diverted at peak periods, and run down at a controlled rate when the flow has moderated.

For process waters, tanks are used for this purpose but for surface water drainage, open lagoons may be used.

III.2.3. PRIMARY TREATMENT – GRAVITY SEPARATION

Primary treatment facilities are separators which, like any settling facility, provide an environment in which suspended solids can be settled coincidentally with the separation of oil in the influent. Flow rate, oil gravity and effluent temperature are factors affecting their design. They are facilities which will separate free oil from waste water but will not separate soluble substances, nor will they break emulsions. Despite their relative simplicity, most of the oil in the effluent will be recovered at the primary treatment stage and is recycled to the process units.

A pre-separator (pre-sedimentation basin or sludge trap) may be provided upstream of a gravity separator where heavily polluted influent streams are present, its primary function being to allow the removal of gross oil and settling of solids which would otherwise impair the performance of the downstream separator basin.

III.2.3.1. Design Principles

In an ideal separator, the principles governing design may be expressed mathematically and although there is a practical limitation to separator effectiveness due to the varying factors involved, the design rules can still be followed for new designs or in assessing the performance of existing designs.

For oil separation, the rising velocity of an oil droplet of given size has to be equal to or greater than the "overflow rate". The overflow rate being the flow rate through the separator divided by its surface area.

The rising velocity of an oil droplet can be determined using Stokes' Law, involving the diameter of the oil droplet; the density of influent; the density of oil in the influent; the absolute viscosity of influent and acceleration due to gravity.

It should be noted that the efficiency of oil removal and hence the actual effluent quality in milligrams per litre at the outlet of a primary treatment facility is influenced by factors which cannot always be controlled or measured.

III.2.3.2. American Petroleum Institute (API) Separator

An API is the simplest form of separator, the separating chamber simply consisting of an open rectangular basin. The standard API separators existing in many refineries comprise an inlet section and oil-water separation chambers. The approach channel and transition part are usually constructed in at least two bays in order to facilitate their cleaning and repair when required. Flight scrapers may be installed to gently move the sludge to a sludge collection pit and oil to the oil skimming device. Covers may be installed to reduce odour and emissions to the air of Volatile Organic Compounds (VOC).

The main advantage of the API separator is that its large volume can intercept large slugs of free oil and solids. This factor helps to improve the performance of the downstream stages. Its main disadvantages are that it requires a large area of land and can only remove comparatively large oil droplets. Design performance data for an API separator are shown in **Table AIII.1**.

III.2.3.3. Parallel Plate Interceptor (PPI)

A PPI is a gravity separator equipped with plates parallel to the current to promote laminar flow and reduce the separation distance. Within a PPI the combined surface area of the plates is significantly higher than the surface area of the conventional API separator, resulting in a smaller ground area. The main disadvantage is that the plates are susceptible to fouling and hence there is an increased maintenance requirement.

III.2.3.4. Corrugated Plate Interceptor (CPI)

In the CPI, specially designed corrugated plate packs are placed counter current to the flow, i.e. the effluent flows downward whereas the oil flows upward to the surface. The advantages are a small surface area and increased efficiency over API and PPI equipment as the CPI can remove smaller oil droplets. The disadvantages are again the possibility of fouling and increased maintenance.

The CPI is particularly suitable for installation on individual processing areas, as close as possible to the point of waste water generation. In these circumstances, there is less likelihood of fouling, the oil may be able to be recycled directly to the unit, and the load on the site effluent treatment plant is reduced.

III.2.3.5. Break Tanks

A break tank provides sufficient residence time to allow light oil to float to the surface of the tank for subsequent skimming and also to allow heavier than water oil and sediments to sink to the bottom of the tank for removal as sludge.

Floating skimming facilities which permit the removal of oil independent of tank level allow the tank to be used for flow balancing purposes.

The break tank can be difficult to incorporate into existing effluent systems using API separators relying on gravity flow without substantial modifications to the system to incorporate collection and pumping stations. Any pumps used in such services must be of low shear design to avoid the formation of oil and water emulsions.

III.2.3.6. Oil Skimmers

Oil collected in the various types of separators has to be recovered. Fixed pipe skimmers are used when the water level in an interceptor is nearly constant at all times. Rotating trough skimmers with hand wheel operation are used in interceptors where the fluctuation in water level is small.

Rotating disc or drum skimmers are used where continuous oil skimming operation is necessitated. These skimmers are available for fixed level and floating application. The fixed level application can accommodate a small variation in water level. Floating skimmers should be considered for continuous or non-continuous operation where large fluctuations in the water level are expected.

III.2.4. SECONDARY TREATMENT- FLOTATION

Flotation devices are forms of enhanced gravity separation which rely on the formation of weak bonds between gas (usually air) bubbles and oil and solid particles. The air bubbles provide the necessary buoyancy to float the oil and solid particles to the water surface for skimming.

There are two main types known as Dissolved and Induced Air Flotation (DAF, IAF). They are generally installed down stream of gravity separators as a secondary treatment prior to a biological process. Designed and operated correctly, they are capable of separating and removing virtually all free oil from an effluent stream and can significantly reduce the concentration of suspended solids, but as with normal gravity separators, they will not separate out soluble substances (design performance for a number of installations are shown in **Table AIII.2**). As secondary devices they will not handle gross free oil successfully.

Both devices rely upon chemical additives in the form of flocculants and/or polyelectrolytes to function efficiently. Modern units generally no longer use iron sulphate for the flocculation/coagulation process but instead rely upon organic polyelectrolytes. Cationic polymers tend to be more effective in removing oil whilst solids are usually better handled by anionic polymers. Water chemistry has a significant role to play in the effectiveness of individual polymers and a number of trials are usually required to select an optimum formulation.

The skimmings, produced as a fairly stable oil - water - solid emulsion, can be difficult to handle and may require additional treatment prior to recycling or disposal. An added benefit of air operated flotation units is that they increase the dissolved oxygen content of the effluent.

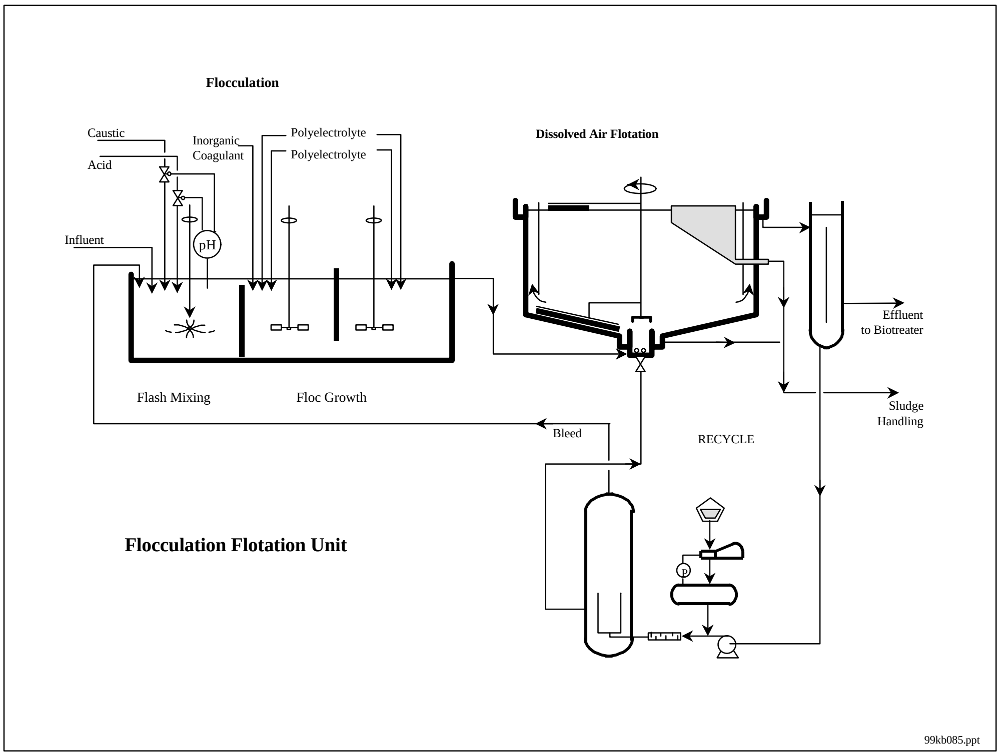
III.2.4.1. Dissolved Air Flotation (DAF)

There are numerous configurations of dissolved air flotation units available, but they all form the fine air bubbles necessary for flotation by releasing into a quiescent zone, wastewater previously saturated with air at approximately 5 - 7 bars pressure. A typical unit is shown in **Figure III.1**.

A proportion of the treated wastewater flow (30% being reasonably typical) is routed to a pressure vessel for air saturation. The saturated wastewater is released into the base of the main treatment tank via an appropriately designed distribution network, allowing the resulting fine air bubbles to flow uniformly through the total wastewater flow. Residence times in the main tank can vary considerably between 30 minutes and several hours. However the emphasis is on maintaining the main tank as a quiescent zone where the skimmings can be removed without undue disturbance. The design of skimmer depends very much on the main tank configuration. Traditional rotating skimmers are used with circular tanks. Similarly configured scrapers are used to remove any heavy sediment and oil from the bottom of the tank. The depth of the main tank varies considerably between proprietary designs.

Virtually all dissolved air flotation units incorporate pre-treatment stages, typically flash mixing where the polyelectrolyte is added, followed by a calming tank where coagulation and flocculation take place.

Figure III.1 Flocculation / Dissolved Air Flotation Unit



III.2.4.2. Induced Air Flotation (IAF)

Induced air flotation units initially found favour on off-shore installations where the small water inventory compared to a traditional DAF allowed for much smaller units which could be readily made gas-tight. IAF units work by using specially designed impellers to induce air into the effluent. Whereas DAF units require quiescent conditions to perform satisfactorily, IAF units form air bubbles and contact them with solid and oil particles under highly turbulent conditions. The resulting froth forms above the impeller in a relatively calm zone.

IAF units generally have four equally sized separation stages with motor operated impeller/inducers followed by a final calming zone from where wastewater is discharged from the unit via a level control valve. Each stage is fitted with a froth skimming device connected to a common skimmings channel. The individual froth skimmers are either weir devices or rotary mechanical skimmers. The unit can be made gas tight if necessary and is fitted with inspection hatches for observation of the skimming process.

Feed pre-treatment is rarely needed with an induced air flotation unit, polyelectrolyte being injected into the feed line at a controlled rate. Wastewater residence times of at least 7 minutes and preferably longer are needed to produce very low to zero levels of free oil at the outlet to the unit. The highly turbulent mixing regime of the IAF makes it essential that the quantities of foaming detergent present in the waste water are kept to an absolute minimum.

III.2.4.3. Waste Production

DAF units produce significant quantities of sludges. The limited information reported in the survey (for three units) indicated an annual sludge production of about 2400 tonnes per year for a throughput of 600 m^3/hour but this figure can be expected to vary widely depending on the type of effluent, the flocculant used, and the way the sludge is removed.

Only one operator of IAF units reported on waste production. In this case, a unit operating at 600 m^3/hour produced 600 tonnes per year of sludge.

III.2.5. FILTRATION SYSTEMS

A filter is a supported bed of granular media (usually sand, anthracite, garnet or a combination of these or nutshells) through which effluent water is passed to remove non-dissolved material. Filters effectively remove un-dissolved oil and solid suspended material from wastewater streams. It may be necessary to add a chemical flocculant such as a polymer to the wastewater prior to granular-media filtration, to enhance removal of free oil and suspended solids.

Granular-media filters can be of different designs. These are differentiated in several ways - mode of operation (downflow or upflow), pressure or gravity, number of media materials in the bed, material of media and depth of penetration of the contaminants.

III.2.5.1. Mixed-media Filters

They are always operated downflow, the particle sizes of the different media are selected so that the media of largest particle size occupies the top layer and the media of smallest particle size occupies the bottom layer. This arrangement results in a large pore size at the inlet-end of the filter to capture and retain a relatively large amount of material from the water without excessive pressure drop build-up, and a small pore size at the effluent-end of the filter to "polish" the effluent by removing fine particles. The different media selected must have appropriate particle densities; the top layer must be the lightest media material and the bottom layer the heaviest.

As impurities are removed from the effluent, the pressure drop across the bed will increase to the point where cleaning is required to allow continued operation and/or prevent breakthrough of oil or solids into the treated water stream. The filters are periodically taken out of service and cleaned by backwashing in the upflow direction to remove the filtered material in order to reduce pressure drop. Backwashing is usually accomplished by first injecting air to break up the bed, expanding or fluidising the bed with water (normally filter effluent) at a relatively high flow rate, with simultaneous air injection to scour the particles, and then flushing with water alone. The nutshell filters do not require air to enhance the cleaning process as they use media scrubbers for this purpose. Note that backwashing may generate significant quantities of oily solids for treatment and disposal.

Filter runs of about 24 hours between washes are normal. If filter runs fall below 8h, it becomes difficult to maintain production and wash water demand becomes excessive.

Conventional filters are characterised by the following disadvantages:

- backwash procedures are complicated requiring proper supervision
- during back-washing the filter is out of operation, requiring additional filters in parallel to maintain operation
- an extensive network of devices (piping, pumps, wash water control, etc.) is needed
- filtration performance is lower just after the backwash (the filter first needs to collect suspended solids for proper filtration) and at the end of the filtration cycle
- a large buffer vessel is required since all the wash-water is collected in a short period.

III.2.5.2. Continuous Sand Washed Filters

In order to cope with these problems several types of filters have been designed, based on continuous sand washing. These use rapid up-flow filtration in which the filtering bed is cleaned continuously. The filter consists of a cylinder-shaped open tank with a bottom cone. The water is fed to the lower part of the bed by a special distributor and passes upwards through the filter bed of sand. The outgoing water is discharged from the upper part of the filter. The sand bed is continuously moving downwards with the help of an air-lift pump that brings sand from the lower part of the filter bed to a built-in sand washer. The sand is mechanically cleaned in the air-lift pump and, thereafter, rinsed in the washer where a small amount of filtrate passes the mechanically cleaned sand counter-currently. The cleaned sand is brought back to the upper part of the sand bed, and the wash water is discharged though a separate outlet.

The advantages are:

- sand washing during filtration within one system requiring little supervision
- continuous low, wash water flow
- stable performance due to presence of a certain level of solids in the sand bed

The disadvantages are:

- the quantity of wash water (5-10% of filtrate) is higher than with conventional filters
- contamination of filtrate might occur as the sand washing system is within the filter.

III.2.5.3. Gravity Filters

Gravity filters have not been used as extensively as other techniques in refinery effluent systems.

III.2.6. TERTIARY TREATMENT - BIOLOGICAL SYSTEMS

The biological treatment of effluent water is based on the process in which a mixed population of micro-organisms use as nutrients substances that contaminate the water. This is the same mechanism by which healthy natural waterways, such as rivers and lakes, purify themselves. This basic process has been intensified and accelerated to give a wide range of treatment plant systems for treating refinery effluent water.

Effluent water containing polluting material is brought into contact with a dense population of suitable micro-organisms for a time sufficient for the microbes to break down the contaminants. The pollutants are adsorbed into the microbial mass, typically oxidised, and partly converted into new cell material. Since free oil is inhibitory to these processes, the feed to biological treatment plants should not contain more than typically 15 to 20 mg/l free oil. Biological treatment plants are thus usually installed after primary and secondary oil removal facilities.

Micro-organisms, and hence treatment plant types, can be divided into those that need oxygen for growth, called aerobic, and those that do not, called anaerobic. Normally, aerobic micro-organisms obtain their oxygen from the free dissolved oxygen present in the effluent, but some organisms are able to obtain it from dissolved inorganic compounds when there is no free oxygen left: this is described as an anoxic process.

Combinations of these processes are able to remove most of the pollutants of concern in refinery effluents. Aerobic processes remove a wide range of carbonaceous material, typically characterised in terms of the associated oxygen demand (e.g. TOD/COD/BOD or TOC) and individual compounds such as phenols, ammonia and sulphide. Anoxic treatment can also reduce levels of Total Nitrogen. Anaerobic treatment is generally not applicable to the low concentration of contaminants typically found in refinery waste waters.

There are many different ways to engineer a biological treatment plant, with a broad classification dependent upon the physical state of the microbial population. In dispersed growth processes (e.g. Activated Sludge processes, see **Section III.2.6.1**), the micro-organisms and effluent water are kept in intimate contact by mixing, with the mixing apparatus usually responsible for keeping the suspension aerated if required. In fixed film processes (**Section III.2.6.2**), the micro-organisms are immobilised or attached to an inert support which is maintained in contact with the incoming effluent. The main operating concerns, which are common to both types of processes, include hydraulic residence/cell contact time, biological mass concentration and age, aeration requirements, temperature, and waste bio-sludge separation for recycle and disposal. These have a marked effect upon treatment plant costs.

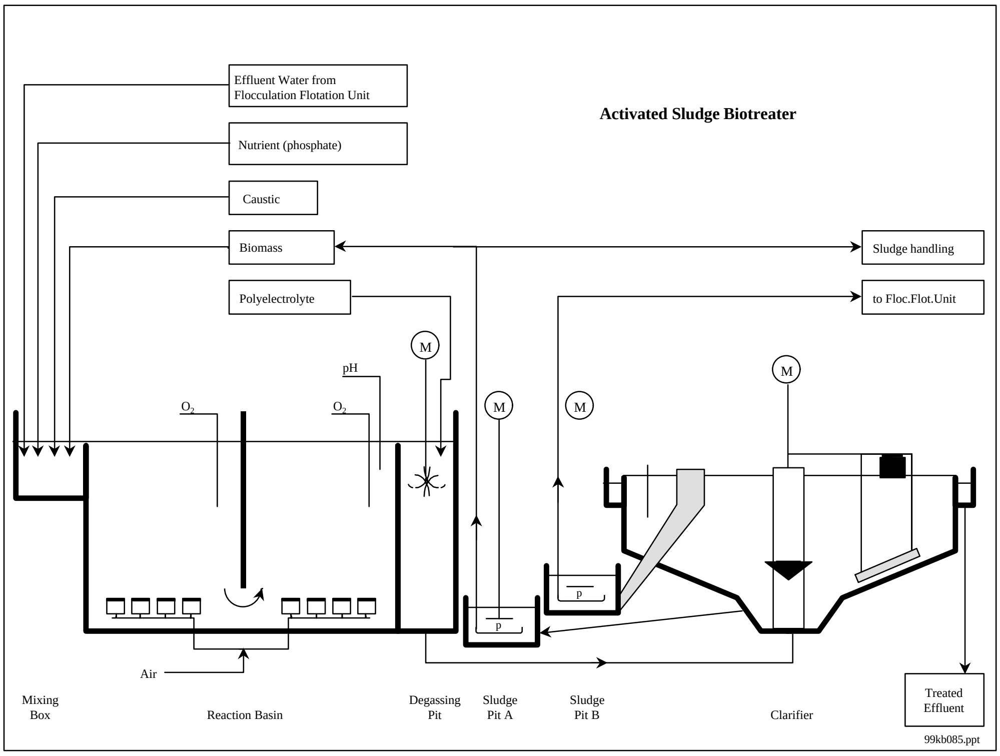
The following are respectively the most common examples of each system, and are frequently installed as part of the total refinery effluent treatment process.

III.2.6.1. Activated Sludge (AS) Process

The activated sludge process is a dispersed or suspended growth system comprising a mass of micro-organisms constantly supplied with organic matter and, for aerobic treatment, oxygen. The micro-organisms grow in flocs, and in aerobic treatment, these flocs are responsible for the transformation of organic material into new bacteria, carbon dioxide and water, and for ammonia reduction into nitrite and nitrate. In anoxic treatment, the nitrate and nitrite are further reduced to gaseous nitrogen. The flocs are constantly being washed out of the reaction vessel to the secondary sedimentation tank or clarifier by the flow of effluent. Here they flocculate and settle under quiescent conditions. It is a characteristic of the activated sludge process that a proportion of this settled sludge is recycled back to the mixing/aeration tank to provide sufficient biomass for contaminant removal. Any excess biological solids are removed, dewatered, and sent for disposal.

There are a large number of variations of the activated sludge process, but a common design is shown in **Figure III.2**.

Figure III.2 Typical Activated Sludge Process



The designs vary only in three principal ways: method of oxygen supply/biomass mixing; loading rate, and mixing/aeration tank configuration. Oxygen can be supplied by diffused air equipment (e.g. bubble diffusers), mechanical aerators (both surface or submerged), or from pure oxygen injection devices. The loading rate is determined by the degree of treatment efficiency required to satisfy effluent discharge consents, and is affected by both the hydraulic residence time in the reactor/clarifier, and contaminant to micro-organism relative concentrations. Mixing/aeration tanks come in a wide range of options including batch/plug flow, and completely mixed regimes, and can be carried out in conventional tanks, shallow oxidation ditches, or even underground shafts.

III.2.6.2. Biosupport Media Systems

In these processes, the micro-organisms that are responsible for degrading the dissolved organic compounds in the incoming wastewater are not suspended in the system, but are provided with some sort of attachment surface. Biosupport media systems can be divided into several categories including:

Suspended Media Systems

These are variations on the traditional activated sludge process. The media to which the micro-organisms are attached is allowed to circulate freely with the effluent being treated. Typically used support packing includes small plastic rings, sponge balls, and activated carbon granules. The use of the packing permits a higher concentration of biomass to be used in the reactor vessel, and hence give a more intensive process.

Fixed Bed Media Systems

In these processes, the media form a fixed bed (similar to a granular filter bed) and effluent water passes either upflow or downflow through the biomass retaining media. Media used in these applications includes activated clay or silica granules. These systems allow a high degree of filtration to give an effluent low in suspended solids. A key operating difference is that the media is periodically expanded and backwashed to remove excess biomass build-up.

Rotating and/or Submerged Biological Contactors

In these systems, discs of media are rotated through the water being treated, and the micro-organisms grow on the surface of the contactors. Aeration in these cases may be provided by either contact with air during the period when the disc is out of the water, or by diffuse aeration provided in the water itself.

Trickling Filters

A trickling filter is a vessel filled with permeable media such as lightweight plastic rings, or a structured packing such as tubes or corrugated blocks. Effluent water is distributed mechanically over the media and percolates down the filter to an underdrain collector. A microbial film develops on the surface of the media to degrade the contaminants. Air circulates through the void spaces via inlet draught tubes at the base of the filter.

Process Selection and Economics

Biosupport media systems generate the same type of waste biomass as the activated sludge process. The economics of process selection depend very heavily on site specific parameters such as wastewater characteristics, type and degree of treatment required (e.g. BOD/COD reduction, ammonia removal, and suspended solids limits). The space and manpower requirements for many fixed film processes are significantly less than those for the traditional AS process. However, the suspended and fixed bed media systems have not found significant use in the petrochemical industry due to the ability of the standard activated sludge process to meet effluent discharge requirements. In many cases, the cost of the media itself even for a small application can be in excess of one million EUR. For the fixed bed systems, equipment for backwashing the media beds is also required, as is also a means for treating the backwash water.

III.2.6.3. NITRIFICATION / DENITRIFICATION

Refinery biological treatment plants are typically designed to remove only organic carbon compounds. Some are designed to remove ammonia also (nitrification) if there is a particular concern over ammonia toxicity in the receiving watercourse. For discharges into sensitive waters with a risk of eutrophication, it may be necessary to remove most of the nitrogen compounds present in the refinery wastewater (denitrification). As mentioned previously (**section III.2.6**), biological processes can be designed to remove ammonia and inorganic nitrogen compounds. Ammonia is converted biologically into nitrite and nitrate by a process termed nitrification. If nitrogen removal is required, the nitrite and nitrate are converted to gaseous nitrogen by a biological process termed denitrification.

Most of the biological systems discussed earlier can be engineered to maximise the degree of nitrification/denitrification within the overall biological treatment process train. The treatment conditions, such as air requirements, biological sludge age, and effluent residence time need to be matched to the requirements of the bacteria being used and the total nitrogen loading. There are many combinations and configurations possible to achieve this. For example, some treatment schemes can have separate treatment stages for each part of the different biological processes, whilst others can have a combined system with only changes in operating conditions.

The addition of extra nitrifying/denitrifying stages to an effluent treatment plant increases the complexity and hence the cost of the installation significantly. These biological processes are also inherently more difficult to control, and this adds to the operating costs.

III.2.6.4. Design Performance and Waste Production

The design performance of a number of activated sludge plants are presented in **Tables AIII.3 and AIII.4** which are for these plants alone and combined effluent treatment plants respectively. The average production of biosludge (17 units) was reported as about 1700 tonnes per year at an average throughput of 250 m^3 per year. This figure varies widely depending on the effluent type, method of operation and water content of the sludge.

III.2.6.5. USE OF MUNICIPAL SEWAGE TREATMENT WORKS

In a small number of cases, refinery effluents are treated in municipal sewage treatment works. In these cases, the effluent will normally be given primary and secondary treatment at the refinery to remove free oil before it is passed to the works. There can be advantages to both parties in such treatment in that the domestic sewage provides nutrients, and dilutes any surges of chemicals which are toxic to the biomedia. The municipal plant can benefit by receiving a reasonably constant flow to balance out peak loads. However, such systems are not universally appropriate and need careful design.

There are also a few situations where refinery effluent is treated in a common user plant serving a number of industries. Similar considerations to the above apply.

III.2.7. MEMBRANE SYSTEMS

Membrane systems are used to remove submicron suspended solids and dissolved solids from a water stream so that it can be discharged or reused. The simplest membrane systems act as a crossflow filter keeping particles too large to pass through on one side of the filter and letting "cleaned" water pass to the other side. Ultrafiltration processes are pressure driven systems across a membrane, typically operated at relatively low driving pressures (10 bar), to remove colloidal materials and large molecules.

III.2.7.1. Reverse Osmosis (RO)

Reverse Osmosis (RO) is a process for removing dissolved solids by applying pressure (up to 70 bar) to drive clean water through a semipermeable membrane, leaving most of the dissolved ions in the original water stream being treated, which thus becomes a concentrated brine solution that must be disposed of. The membranes are typically either hollow fibre or spiral wound, but an RO system requires many elements besides the membranes themselves, including intake and pre-treatment facilities and pressurisation.

In order to minimise membrane fouling, pre-treatment, typically consisting of more than one technology, is needed to remove suspended matter, bacteria, and ions that could precipitate. Significant costs are associated with pre-treatment required to make the inlet water suitable as RO feed. Problems that need to be addressed are membrane scaling, device plugging, colloidal fouling, and biological fouling. In some cases these also require the addition of chemical treatments to the water to avoid the problems from occurring. Finally significant environmental concerns and costs can surround the disposal of the concentrated brine which in virtually all cases will be more acutely detrimental to the environment than the stream before concentration.

There is little operating experience in the use of RO systems for the treatment of refinery wastewaters and none were reported on in this survey. Of particular concern are dissolved organics and biomass which must be removed from the feed water to prevent coating and fouling of the membranes. Appropriate wash cycles and chemicals are not yet well understood for this application.

Since even under the best pre-treatment regimes and chemical treatment programs membranes will foul and deteriorate in performance without cleaning, RO systems must also be designed with the facilities for and redundant capacity to provide for taking modules offline and mechanically or chemically cleaning them, which can involve several different cleaning steps (i.e. acid and base, etc.). For these reasons, RO systems are not normally used for effluent treatment processes and they tend to be expensive due to the high power requirements for the energy to drive the high pressure feed pumps.

III.2.7.2. Electrodialysis (ED)

Other forms of membrane treatment are Electrodialysis (ED) and Electrodialysis Reversal (EDR). In this application, the ionic compounds in a solution are removed through a semipermeable membrane by the use of electrodes that introduce an electrical potential in the solution causing the cations to migrate to the negative electrode and anions to migrate to the positive electrode. Due to the spacing of the membranes, regions of dilute and concentrated salt solutions are isolated. As with

RO the feedwater quality must be very high for ED and EDR in order to avoid the same membrane fouling problems mentioned above. EDR uses polarity reversal to help control membrane scaling and fouling.

No electrodialysis units were reported on in this survey.

III.2.8. SOUR WATER STRIPPERS (SWS)

Overhead drum waters from distillation columns and vacuum unit ejector condensate may contain significant quantities of dissolved hydrogen sulphide and ammonia.

These contaminants are most commonly removed in a stripping column which may be heated with steam or other heating medium. Live steam may also be used as a stripping medium. Sour water strippers operate at relatively low pressures (generally 1-2 Bar) and may contain thirty or more distillation trays depending upon the desired concentration of hydrogen sulphide and ammonia in the treated water.

All elements of the design need to consider the high potential for fouling in this service and it is common, as an additional measure to inject antifoulant chemicals into the sour water feed. A pH control system is also required to ensure optimal removal of the contaminants.

The overhead gases from the stripper column are either incinerated or routed to sulphur recovery units for combustion in burners specially designed to avoid excessive NOx production from the combustion of ammonia.

Design performance for a number of recently installed sour water strippers is presented in **Table AIII.5**.

III.2.9. STORM AND FIRE WATER CONTROL

Prevention of uncontrolled discharges is essential for proper refinery operations within both existing and new plants. Where appropriate, extra controlled discharge facilities (e.g. storm tanks / basins) may be installed as a means of controlling the discharge of heavy falls of rainwater and water used for fire fighting. Their function is to allow retention of the water for inspection and testing of quality before a decision is taken on whether to discharge directly to the receiving water or to route it back for further treatment.

Such facilities may include a first flush compartment and hold up for storm water to cater for the effluent which occurs as a result of the 'first rain' after a relatively dry period and further compartments for following rainfall.

The pumping capacity to transfer contaminated effluent from the controlled discharge facility to secondary treatment should be based on the available intake capacity of the secondary treatment facility, whilst considering the need to sufficiently empty the controlled discharge facility before the next rain event.

III.2.10. AIR EMISSIONS FROM WATER TREATMENT

The sewer system and the waste water treatment in a refinery may be sources of odour nuisance and hydrocarbon emissions particularly from open drains and from oil separators. These emissions are generally low and only of local importance: the CORINAIR Emissions Inventory [5] listed the following low contribution (**Table III.2**) to total emissions of the 1990 inventory (for 28 countries) for the global waste water treatment in Industry, Residential and Commercial sectors (SNAP code 09100) and sludge spreading (SNAP code 091003):

Table III.2 CORINAIR Emissions Inventory Figures

code 09100	CH_4	0.5%
	NMVOC	0.1%
	NH_3	0.2%
	CO_2	0.1%
	N_2O	0.5%
code 091003	CH_4	0.3%
	NMVOC	0.1%
	NH_3	0.1%

(NMVOC = Non methane volatile organic compounds)

These emissions mainly result from the following processes:

- sewers
- primary separation
- secondary flotation / filtration
- tertiary biotreatment
- sludge storage
- landfill and landfarming

They may be reduced in existing refineries by converting open drains to closed piping systems and by covering the primary separators. Neither may be as simple as it sounds. Drains have to be able to carry all the flow under extreme conditions and covers on separators may impede their operation, particularly the skimming of oil and monitoring of their performance. For separators, the highest emissions are likely to come from the inlet bay, and sometimes only this is covered. Alternatively, particularly in new installations, the primary separators may be replaced by enclosed tanks similar to those described under Break Tanks (see **Section III.2.3.5**).

Waste waters from processing which may have absorbed low-boiling and often odorous materials (e.g. NH_3, H_2S), are normally treated by stripping with steam or gas before entering the effluent system (See **Section III.2.8**). Emissions from sludges can be minimised by appropriate handling and management procedures.

Information on various items of such equipment installed recently in European refineries is presented in **Table IIIA.8**.

III.3. SLUDGE MANAGEMENT METHODS

Waste generation, treatment and disposal in oil refineries were the subject of a previous CONCAWE report [3] which should be consulted for data on the complete range of refinery wastes. The main effluent treatment sources of sludges are:

• sewers	grit and solids
• primary separation	oily solids
• secondary flotation / filtration	oil / water / solid emulsions
• tertiary biotreatment	Excess biological solids

III.3.1. PREVENTION

There are a whole range of activities employed in oil refineries to prevent the production of sludges. These are described in **Section IV** of the combined report.

III.3.2. RECYCLE AND REUSE

In the last decades, the quantity of waste from the oil industry which is recycled and reused has grown and continues to do so. The methods applied vary with the type of waste, e.g. for sludges, recovery of oil during treatment. The aim of the recycle and reuse methods is to reuse the waste for its original purpose or to find an alternative use for it to avoid its final disposal. Therefore, waste production is reduced while natural resources are conserved and/or protected. One such alternative use can be to provide energy via combustion. This is discussed further under the topic of incineration.

III.3.3. SLUDGE REDUCTION PROCESSES

In the current survey, information was obtained on a number of processes used for treating sludges. Only these processes are considered here.

The sludges recovered from the various effluent treatment processes described in **Section III.2** vary widely in their properties. Those from gravity separators and flotation systems are usually oily and have a high water content. Biosludges usually only have a very low oil content but typically have a very high water content. Depending on the disposal route adopted, these sludges are often treated before disposal.

Treatment methods are used for two main purposes:

- to reduce the quantity of waste requiring disposal
- to recover the oil for recycling

A large proportion of refinery sludges are treated for one or both of the above reasons.

The choice of whether to treat and if so which treatment to use depends on many factors including the composition of the sludge and the choice of disposal route. For example, if the sludge is to be used as a fuel, it will be important to remove the water, but not the oil. Alternatively if a biosludge which is essentially oil free is to be spread on land, it may be preferable to leave it wet.

III.3.3.1. Centrifuges

Centrifugation exploits the difference in density between solids and liquids (or two liquid phases) to separate them by applying centrifugal force.

Two main types of decanter centrifuge can be applied at refineries: 2-phase, which yields a solids cake plus a single effluent stream (mixed oil and water); and 3-phase which, as the name suggests, yields separate oil and water streams, as well as the cake.

Advantages of decanter centrifuges include resource recovery, flexibility and high volume reduction. With good operation, cake suspended solid contents of 20-40% can be achieved.

Information on Centrifuge units used recently in refineries can be found in **Table III.A6**. In many cases, refineries do not own centrifuges but employ a contractor to periodically bring equipment to the site when there is sufficient sludge collected to treat economically. Such cases are indicated by an “L” in the table.

III.3.3.2. Filters

Filter presses and related systems, mechanically dewater sludges (and similar materials) by pressure. The benefits are high volume reduction and recovery of oil from oily sludges. In most cases, filter aids (e.g. diatomaceous earth, proprietary cellulose-based products) are needed to enhance dewatering and prevent clogging of the filter but will increase waste volumes. Heating and flocculants may also be used to enhance performance.

Belt filter presses can produce a 15-20% suspended solids filter cake but have high maintenance requirements and can have problems with the processing of oily sludge due to filter cloth blockage.

In plate and frame presses the sludge is mechanically squeezed in filter-cloth lined chambers. Fully automated plate and frame presses are available, but at a much higher capital cost. They have the advantage of relatively simple operation and can produce a very high solids cake (30-50% is certainly feasible) but suffer from filter cloth blockage (especially with oily sludges).

Information on Filtration units used recently in refineries can be found in **Table III.A7**.

III.3.4. SLUDGE DISPOSAL METHODS

III.3.4.1. Landfill

The term "landfill" covers a range of activities involving the disposal of wastes on to or into land. The general principle is to deposit wastes either in specially excavated or pre-existing depressions in the ground or specially prepared sites above ground. After deposition, the wastes are covered with soil and the land is rehabilitated.

A number of refinements are possible to this basic procedure, depending on the geological conditions at the site and the degree of hazard exhibited by the waste. It is now common practice, before filling, to line the bottom with an impervious membrane of either compacted clay or polymer, or both. This serves to stop contaminants leaking out of the landfill. A similar impervious layer is also often used to prevent the ingress of rain water.

Some European refineries have their own landfill sites. These are controlled under European and national waste legislation. However, for most refineries, material for landfill will go to a commercial, a state-run or an industry co-operative waste disposal facility.

Waste is often pre-treated before disposal (**section III.3.4.4**) to landfill, e.g. by dewatering or solidification. While dewatering reduces the volume of waste, solidification is designed to bind the constituents together and prevent leaching.

III.3.4.2. Landfarming

Landfarming is the treatment of oily or biological sludges by controlled application to a specially prepared area of soil so that the micro-organisms present can biodegrade the organic components of the sludge as rapidly as possible.

As performed in the past, landfarming had perceived risks of contaminant accumulation and dispersal that could result in environmental damage. These risks can be eliminated by use of contained facilities (either engineered or by natural geology) and well-defined operating procedures.

III.3.4.3. Incineration

Incineration is high temperature oxidation which converts oily sludges etc. into gaseous products and solid residues (ash) which are less voluminous than the original materials. There are many types of incinerator available providing a potential disposal route for many refinery wastes. The variety of wastes for disposal requires versatile incinerators, or the use of a range of types. Materials which are basically hydrocarbons can be burned in modified boilers as fuel. Alternatively, oily materials can be incinerated in power station boilers or cement kilns. Less combustible or more hazardous materials may require the use of a support fuel and/or the installation of expensive flue gas scrubbing/solids removal equipment to meet air pollution regulations.

Incinerators have been installed in some European refineries, while others utilise co-operative, commercial or municipal incinerators for the disposal of some wastes.

III.3.4.4. Sludge Stabilisation

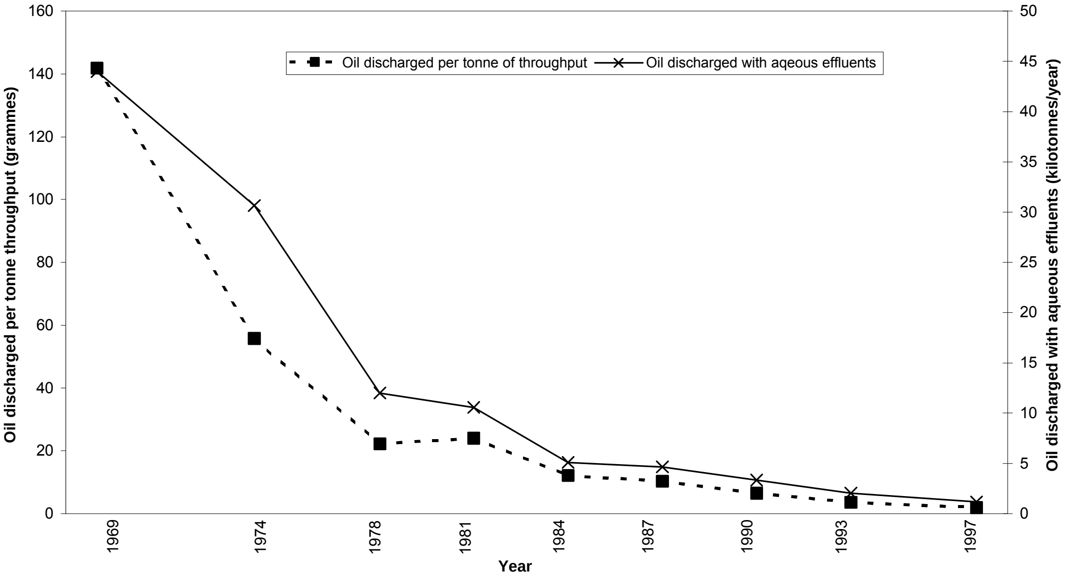
Sludges are often stabilised before disposal. This involves mixing the sludges with other materials which serve to immobilise the oil and reduce the possibility of leaching. The usual material for this is lime, but other materials such as cement, fly ash and spent FCCU catalyst are also used. The addition of stabilising materials generates an increased volume for disposal. It is often combined with mechanical dewatering.

III.4. QUANTITIES OF EFFLUENTS, OIL IN EFFLUENT, SLUDGE AND WASTE GENERATION

III.4.1. OIL IN EFFLUENTS

CONCAWE regularly carries out a survey of effluents from Western European refineries, the latest of which was in 1998 for 1997 results. [4] In this survey, 105 refineries operating in Western Europe reported their results. The total volume of effluents was 2942 million tonnes of which 2629 million tonnes was cooling water. leaving about 313 million tonnes of process, storm and ballast water. After treatment, the total weight of oil discharged was reported at 1168 tonnes of oil, an average oil content of about 3.7 mg/l on the volume of process, storm and ballast water. The series of surveys demonstrates a dramatic reduction in the quantity of oil discharged over the period as shown in **Figure III.3**.

Figure III.3 Trend of Oil Discharged in Refinery Effluent



Of these 105 refineries, 6 had only primary treatment, 7 had primary and secondary treatment, and the remaining 92 had some sort of tertiary treatment as well.

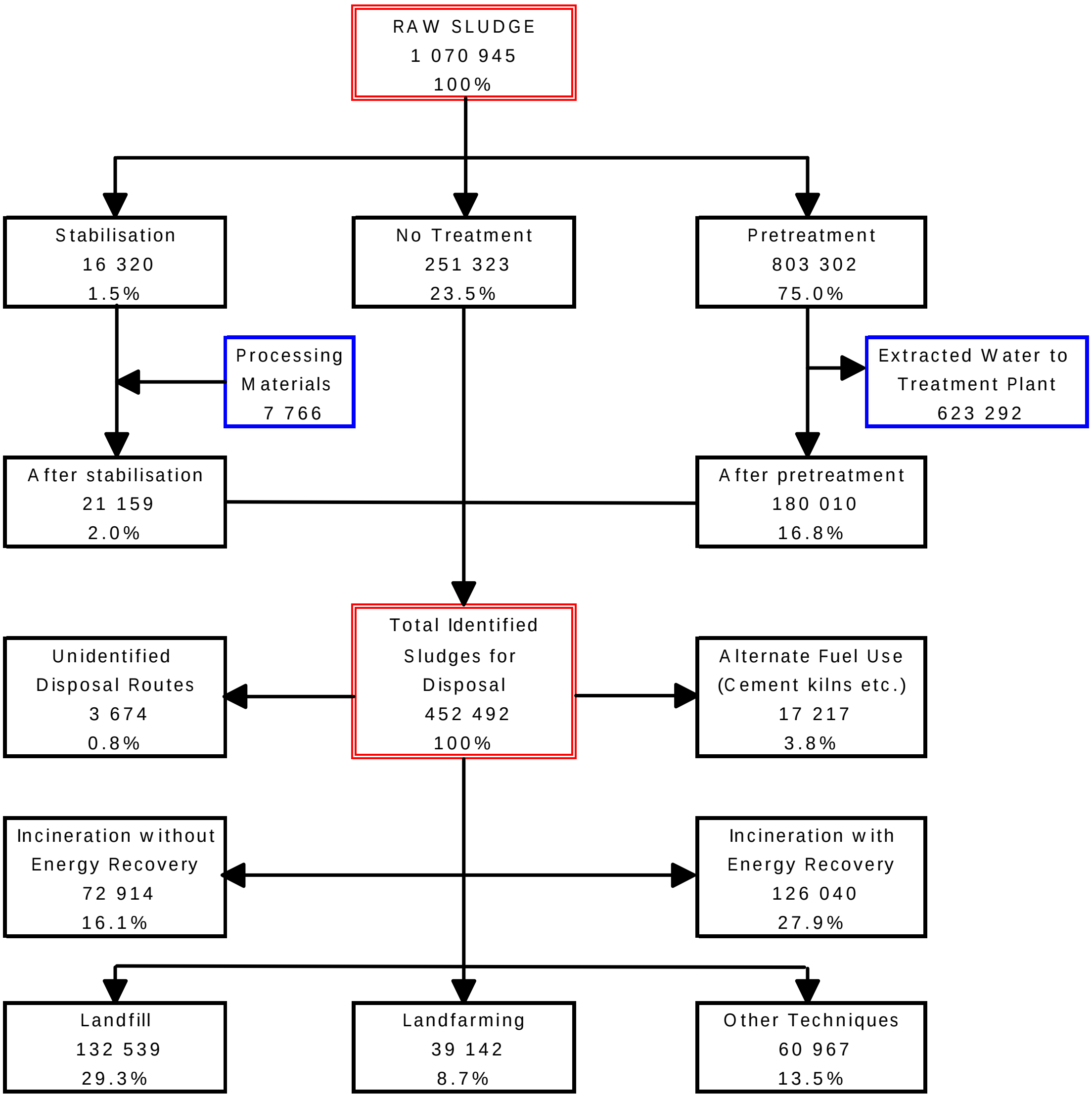
III.4.2. SLUDGES

The sludges reported as generated from effluent treatment in European refineries in 1993 totalled 775 000 tonnes comprised of:

- 450 000 tonnes from physical separation
- 325 000 tonnes from biological treatment

Of this about 580 000 tonnes was pre-treated before disposal to give 130 000 tonnes of treated sludge. For treatment and disposal purposes, effluent treatment sludges are often mixed with sludges from other sources in refineries. The previous CONCAWE survey [3] looked at the total picture of sludge management. This is summarised in **Figure III.4**

Figure III.4 Summary of Refinery Sludge Arisings and Disposal Routes.



All weights in tonnes

III.5. COSTS

III.5.1. CAPITAL COSTS OF EFFLUENT TREATMENT

The determination of the capital costs of wastewater treatment is not a simple matter of just identifying the purchase cost of equipment, but rather must also take into account the costs of engineering design, civil engineering works, site preparation (which may include disinvestment and disposal of existing facilities), and actual construction and installation. These costs often significantly exceed the cost of purchased hardware. As these factors can vary significantly depending on local circumstances, it is difficult to make comparisons between different refineries and quoted costs can vary considerably.

Table III.3 below documents the actual reported costs associated with the listed technologies as installed since 1990 in European refineries. Data from before this year were excluded to ensure that only plants built to a modern standard were considered. As far as possible, the effects of inflation in the years 1990 to 1996 were included. As costs were quoted in a wide range of currencies, these were converted to ECU (and subsequently to EUR) using the exchange rates existing in February 1997. These data are presented in more detail in the tables in **Appendix III**.

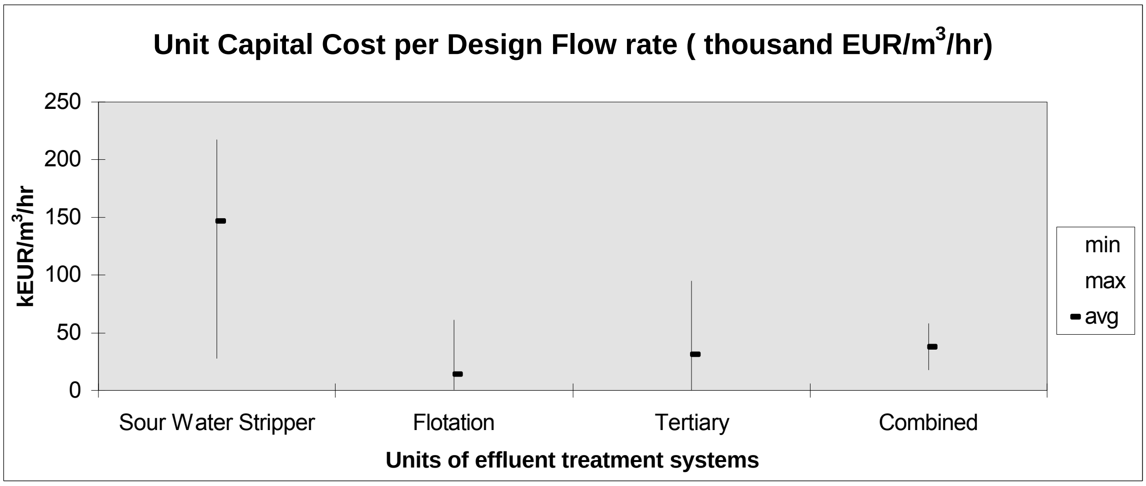
Table III.3 Installed Capital Costs of Effluent Treatment Plant

Technology*	Design Flow Rate (m^3/hr)	Design NH_3 (mg/l)**	Design Oil (mg/l)**	Design BOD (mg/l)**	Capital Cost (EUR)
Sour Water Stripping	20 to 50	10 to 100	NA	–	3 to 11M
Primary Separators (1)	1 200	NA	NA	NA	2.2M
Secondary Flotation – DAF	300 to 800	NA	40 to 80 (2)	NA	1.6 to 1.8M
Secondary Flotation – IAF	400 to 820	NA	1.5 to 10 (2)	NA	0.5 to 2.1M
Tertiary- Non-Nitrifying Biox	80 to 500	25 to 40	5	20 to 105	2.7 to 5.6M
Tertiary - Nitrifying Biox	60 to 500	2 to 5	5	10 to 15	4.8 to 16.3M

Notes:
* Data from European Refinery installations 1990 and later unless otherwise stated.
** Maximum design effluent concentrations
(1) – Data from only 1 non-European refinery available in period of data collected
(2) – Numbers reported are average actual effluent.
M = Million
NA = Not Applicable

Capital costs obviously vary with the design throughput. With the limited data available, it was not possible to draw any firm conclusions on this variability. **Figure III.5** below shows that for the various types of unit, a wide range of costs was reported.

Figure III.5 Variation of Capital Costs with Design Flow Rate



Examples of the actual costs of installing additional effluent treatment processes in the 1990s at two existing refineries which are in the same EU member state are presented in **Tables III.4 and III.5**. The units were designed to handle similar flows. The costs can be compared with each other and with the costs of the individual items given in the tables in **Appendix III**.

In Case A, which is an old refinery, new secondary and tertiary treatment were both installed, but considerable extra works were also required to bring the drainage system up to modern standards. **Table III.4** shows that the installed costs of the two main units was 18 million EUR. Even though this includes civil engineering costs which raise the price well above the unit costs, it still represents only about 40% of the overall project cost of about 44 million EUR.

Table III.4 Actual Cost of a Complete Effluent Treatment Project – Case A

Item	**Capital Cost (million EUR)**
Flotation Plant	5.4
Activated Sludge Plant	12.6
Total new effluent treatment	**18.0**
Upstream Preparatory Work	3.9
Pre-collection Modifications	0.6
Underground Piping	4.9
Storm Surge Provision	7.5
API Separator Modifications	3.6
Balancing Facilities	1.8
Chemical Dosing	3.6
Total ancillaries	**25.9**
Total for Complete Installation	**43.9**

In Case B, only tertiary treatment was installed. As this was a more modern refinery less additional work was required than in Case A. However, as shown in **Table III.5**, the main unit cost of 10.6 million EUR for the activated sludge plant was still only 56% of the total cost.

Table III.5 Actual Cost of Retrofitting an Activated Sludge Plant – Case B

Item	**Cost (million EUR)**
Activated Sludge Plant	10.6
Sewer Improvements	2.7
Upstream Source Reductions	1.9
Final Polishing, Storm Basin, etc.	3.8
Total for Complete Installation	**19.0**

III.5.2. OPERATING COSTS FOR EFFLUENT TREATMENT PLANT

The operating costs associated with running wastewater treatment plant consist of utilities, chemicals, energy, maintenance, manpower and waste sludge treatment and disposal. **Table III.6** lists these costs reported for European refineries, excluding manpower and sludge management related expenses. The latter costs are reported separately in **Section III.5.4**. Since manpower costs are very much influenced by the country of operation, these have been reported separately (**Table III.7**) in terms of typical man-years of effort for wastewater treatment plants of different levels of complexity. These estimates are based on averages of the numbers reported by refineries and are given both as the average and the range. Readers can apply appropriate labour costs to these values to arrive at representative manpower costs for countries of interest to them.

Table III.6 Operating Costs of Effluent Treatment Plant

Technology*	Design Flow Rate (m^3/hr)	Operating Costs 1997 (per yr)
Sour Water Stripping	20 to 50	50 to 400 k EUR
Primary Separators (1)	1,200	NA
Secondary Flotation – DAF	300 to 800	20 to 130 k EUR
Secondary Flotation – DAF	400 to 820	55 to 130 M EUR
Non-Nitrifying Biox	80 to 500	140 to 900 M EUR
Nitrifying Biox	60 to 500	250 to 850 M EUR

Notes:
* Data from European Refinery installations 1990 and later unless otherwise stated.
(1) Data from only 1 non-European refinery available in period of data collected
NA = Not Available

Table III.7 Typical Operator Effort Required for Treatment Plants:

Treatment Type	Average Man-Years	Range
Primary	1.2	0.5 to 2.2
Primary and Secondary	1.8	0.5 to 3.7
Primary, Secondary and Tertiary	2.7	0.6 to 6

There was insufficient information to draw any conclusions on the manpower requirements of other processes.

III.5.3. COSTS OF SLUDGE PRE-TREATMENT

In 1993 CONCAWE carried out a survey of waste in Western European refineries. [3] In this survey 89 refineries reported their sludge production from all sources as 1.07 million tonnes of which 803 000 tonnes were pre-treated to leave 180 000 tonnes for disposal. The total of treated and untreated sludges for disposal was therefore 450 000 tonnes.

Sludges derived from refinery effluent treatment systems amounted to ca. 770 000 tonnes of which ca. 450 000 tonnes was from primary and secondary separation processes and ca. 320 000 tonnes was from biotreatment. Of this about 580 000 tonnes was pre-treated before disposal to give 130 000 tonnes of treated sludge. The average cost of this pre-treatment was 45 EUR/tonne and the average cost of sludge disposal (all sludges) was 60.5 EUR/tonne.

III.5.4. COSTS OF SLUDGE DISPOSAL

Some up to date information was obtained from a few refineries in a number of the Member States in the survey of costs carried out for this report. These are reported in **Table III.8**.

Table III.8 Typical Costs of Waste Disposal

Waste Type	Range EUR/tonne	Average EUR/tonne
Incinerator Ash	61 to 220	147
Biosludge	14 to 195	55
Oily Sludges	17 to 293	105
All	17 to 293	95

These can be compared with information from the previous CONCAWE Refinery Waste survey. [3] **Table III.9** below summarises the sources, quantities and reported costs of sludge disposal from this report. It can be seen that the average waste disposal cost was some 50% higher in this survey than in the previous one. This probably reflects a real increase in costs due to the higher standards of waste disposal which have been introduced over recent years. However, it must be stressed that these data are based on a much smaller sample than the previous report.

Table III.9 Costs of Sludge Disposal Methods

Pretreatment & disposal		**tonne/yr**
Sludge generated		1 070 945
Sludge to Pre-treatment		819 622
Sludge ex Pre-treatment		201 169
Sludge to Disposal		452 492
Disposal of Sludges by	**%wt**	**tonne/yr**
Alternate Fuel Use	3.8	17 217
Landfill	29.3	132 539
Landfarm	8.7	39 142
Incineration with Energy Recovery	27.9	126 040
Incineration without Energy Recovery	16.1	72 914
Other Disposal Routes	13.5	60 967
Unidentified	0.8	3 673
Total Reported Costs		**EUR**
Sludge Pretreatment		18 930 097
Sludge Stabilisation		1 113 462
Alternate Fuel Use		951 759
Landfill		6 637 871
Landfarm		365 645
Incineration with Energy Recovery		6 719 910
Incineration without Energy Recovery		5 002 196
Other Disposal routes		1 382 635
Total Sludge Management		41 103 574
Average Costs (for sludges where costs quoted)		**EUR/tonne**
Sludge pretreatment		45
Disposal of all sludges by:		
Alternate Fuel Use		137
Landfill		52
Landfarm		12
Incineration with Energy Recovery		110
Incineration without Energy Recovery		92
Other Disposal Routes		25
Average for all disposal routes		63

The variability of disposal costs is illustrated in **Table III.10** which details the quantities of sludges disposed of at ranges of costs of incineration.

Table III.1 Range of Costs for Disposal of Sludges by Incineration

Cost Range for Incineration (EUR/tonne)	Raw Sludge (tonnes)	Treated Sludge (tonnes)
< 20	30	8 425
20 to 45	18 615	2 030
45 to 65	10 656	7 566
65 to 85	9 662	3 844
85 to 110	11 090	4 016
110 to 130	4 988	4 791
130 to 150	4 820	1 378
150 to 175	0	8 822
175 to 215	0	5 835
215 to 260	3 350	40
260 to 350	860	2 291
350 to 435	611	1 806
435 to 865	130	519
> 865	40	395

III.6. COOLING WATER

III.6.1. GENERAL CONSIDERATIONS

The subject of cooling is mainly being covered by a “horizontal BREF”. However, this only gives limited consideration of the topic of contamination of cooling water by the material being cooled.

A wide range of techniques is used for cooling purposes in oil refineries the main ones being air cooling, recirculating water cooling and once through cooling water. Most refineries use a combination of two or even all three of these.

For air and recirculating water cooling, the issues involved are little different for oil refineries than for other industries. These types are therefore not considered further in this document.

With once through cooling however, the possibility exists of contamination of the cooling water by the stream being cooled, and hence the discharge of oil into the aquatic environment.

Out of the 105 European refineries reporting in the CONCAWE survey[4], 38 utilised some form of once-through cooling water. However, not all of these cases can lead to pollution of the surface water by oil. There are a number of possibilities for once-through cooling in refineries including:

- Once-through cooling water is only used for cooling non-polluting streams, e.g. in power generation. In this case, the situation is similar to a power plant;
- Once-through cooling water is used for heat exchange with a recirculating water system which then cools the process streams;
- Once-through cooling water is used to directly cool (via heat exchanges) process streams.

Of these, only the last is liable to lead to contamination of the cooling water and hence of the aquatic environment. Therefore, only this situation is considered further. The CONCAWE survey[4], did not differentiate between these various possibilities.

III.6.2. TYPICAL ONCE-THROUGH COOLING SYSTEM

In a typical system, water is extracted from a surface water body, filtered if necessary and sometimes treated with biocide to inhibit fouling. It is then passed around the refinery where needed and through heat exchangers to remove heat from streams which require cooling. Normally, the effluent water is clean, but occasionally leaks can develop in a heat exchanger allowing oil to pass into the water. To remove this, the cooling water is passed through gravity separators to separate any free oil before it is discharged back to the water from which it was originally taken.

Because of the high flow rates usually used, it is impractical to apply more advanced treatments for the effluent cooling water. Also, the stream is too “weak” to allow biotreatment. However, because the stream is only clean water and oil, and with low suspended solids content, gravity separation is more effective than on the mixed effluent streams to which it is normally applied. This, coupled with the low rate of leaks and the high volume of water mean that cooling water discharges rarely contain more than 1 mg/l oil. Monitoring of the receiving waters around the cooling water outfalls of a number of European refineries has shown that such dilute discharges of oil have no measurable environmental effects.

III.6.3. ALTERNATIVE ONCE-THROUGH SYSTEMS

It is unlikely that any new refinery would be built in Europe with direct heat exchange between oil streams and cooling water which was to be discharged to surface water. However, for existing plants, the situation is more complicated. A refinery cooling system is an integral part of the process and is very difficult to change completely. However, in some circumstances as units are replaced, alternative cooling systems may be provided.

In theory, there are two possible ways in which an existing once-through cooling system could be modified to reduce the chances of pollution of surface water. In both of these, the cooling water system is converted to a closed circuit, but in one case, the water in this circuit is cooled in the conventional way through cooling towers. Such a system is not without environmental problems which are fully addressed in the “horizontal BREF” on cooling. The alternative is to cool the recirculating system by heat exchange with once-through cooling water. The problems arise in this case because of the lower temperature difference between the two streams leading to very large heat exchangers and possible implications for energy efficiency.

III.6.4. COSTS OF REPLACING DIRECT ONCE-THROUGH SYSTEMS

The cost of replacing a direct once-through system with either of the alternatives described **Section III.6.3** above will be highly dependent on the circumstances of the individual refinery. However, the costs would almost certainly be substantial. For example, as long ago as 1987, one large refinery calculated the cost of removing once-through cooling from the primary distillation unit to be ca. 18 million EUR and from the whole refinery to be ca. 100 million EUR. At today’s prices, the cost would probably be much higher. The environmental benefit achieved is extremely unlikely to justify such a cost.

III.6.5. LOSS MINIMISATION

There are a number of actions that can be taken to minimise losses of oil into the receiving water via once-through cooling water as follows.

III.6.5.1. Preventative Measures

Certain designs of heat exchangers are less prone to leakage than others. Such designs are described in the horizontal BREF on Cooling. Corrosion can also be reduced by replacing existing heat exchangers with ones constructed from titanium. Such replacements are costly and would normally be considered only when exchangers are replaced as part of the ongoing maintenance programme.

III.6.5.2. Monitoring

Losses of oil through leaks can also be minimised through continuous monitoring of the cooling water system. At its simplest, this comprises monitoring of the cooling water separators for oil build-up. If this is observed, then it will be necessary to trace back through the system to identify the source of the leak so that corrective action can be taken. Detailed system drawings are essential for this activity. Fingerprinting of the oil can also speed up identification of the leak.

A further refinement is to install oil in water monitors at various points in the cooling water system. This allows leaks to be detected rapidly and corrective action taken. For this procedure to be effective, sparing of critical heat exchangers will be required.

III.7. REFERENCES

1. EU (1996) Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. Official Journal of the European Communities No. L257, 10.10.1996

2. CONCAWE (1990) A field guide on reduction and disposal of waste from oil refineries and marketing installations. Report No. 5/90. Brussels: CONCAWE

3. CONCAWE (1995) Oil refinery waste disposal methods, quantities and costs - 1993 survey. Report No. 1/95. Brussels: CONCAWE

4. CONCAWE (1998) Trends in oil discharged with aqueous effluents from oil refineries in Europe - 1997 survey. Report No. 8/98. Brussels: CONCAWE

5. EEA (1996) Atmospheric emission inventory guidebook. Copenhagen: European Environment Agency

APPENDIX III – TABULATED DATA

Table AIII.1 Primary Treatment

Year Built	Type	Design Flow Rate (m³/hr)	Capital Cost (EUR x 10^6)	Operating Cost/yr (EUR x 10^3)
1974	API	1000	–	1800
1973	API	730	–	–
1965/95	API	300	–	160
1963	API	2400	–	560
1995	API	1200	2.0	–

Table AIII.2 Flotation Units

Year Built	Type	Design Flow Rate (m³/hr)	Capital Cost (EUR x 10^6)	Operating Cost/yr (EUR x 10^3)
1995	DAF	80	0.2	18
1994	DAF	300	1.4	20
1989	IAF	400	2.4	47
1993	DAF	350	8.0	683
1996	IAF	818	0.4	112
1996	DAF	50	3.1	–
1996	DAF	800	1.5	–

DAF	Dissolved Air Flotation
IAF	Induced Air Flotation

Table AIII.3 Activated Sludge Plants

Year Built	Type	Design Flow Flow (m^3/hr)	Capital Cost (EUR x 10^6)	Operating Cost/yr (EUR x 10^3)	Max Design Effluent Concentrations (mg/l)		
					Phenols	BOD	NH_3
1991	Biotreater	12.5	0.3	min.	–	30	–
1991	Denitrification*	60	5.7	219	<0.5	<15	–
1996	Biox (Denite)	500		510	0.1	10	5
1993	2-Stage Biox	80		2 513	3	–	30
1993	Biofilter	500	5.3	126	0.2	20	25
1980/93	Biox (No Denite)	330	6.7	3	0.02	25	15
1967/92	Biox **	286	2.8	797	–	105	–
1993	Biox (Denite)	260	8.6	330	0.24	–	3.2
1996	Biox	230	1.2	66	0.2	25	–
1993	DNB treater	260	17.1	740	–	15	2.4
1996	Trickling Filter	50	3.4	–	<0.35	32	–
1992	Biox ***	–	46.5	–	0.5	35	40
1991	Biox	100	4.8	1 815	–	60	–

* Denitrification

** Includes DAF

*** Unit described as Refinery Effluent treatment but waste generated as “biosludge”

Table AIII.4 Combined Effluent Treatment Plants

Year Built	Type	Design Flow Flow (m^3/hr)	Capital Cost (EUR x 10^6)	Operating Cost/yr (EUR x 10^3)	Max Design Effluent Concentrations (mg/l)		
					Phenols	BOD	NH_3
1960/80	API, DAF, BIOX	600	34.9	796	–	–	–
1991	Stripper, API, Biox	600	10.8	1 145	<1*	5*	–

Table AIII.5 Sour Water Strippers

Year Built	Design NH_3 Effluent Conc. (mg/l)	Actual Performance (mg/l NH_3)	Design Flow Rate (m^3/hr)	Capital Cost (EUR x 10^6)	Operating Cost/yr (EUR x10^3)
1996	18		22	2.7	–
1996	10		30	4.0	21
1992	max 150	13	20	0.6	97
1993	50		25	5.4	43
1995	50	35	32	5.3	175
1992	100		50	10.9	–

Table AIII.6 Centrifuges

Year Built	Sludge Type	% Reduction	Feed Rate (tonne/yr)	Own vs Lease	Capital Cost (EUR x 10^6)	Operating Cost (EUR/tonne)
1996	Oily	74.7	825	L	–	25.8
1972/94	Bio	99.75	18K	O	1	453.8
1992	Oily	75	10K	O		20.9
1991	Bio	77	3K	O		–
–	DAF	96	115K	L		48.9
1985	Bio	86	13.4K	O		4.2
–	Oily Bio	–	530	L	–	–
–	Bio	90	2.5K	L	–	37.7
–	Oily	85	1.2K	L	–	37.7

Table AIII.7 Filtration Units

Year Built	Sludge Type	% Reduction	Feed Rate (tonnes/yr)	Own vs Lease	Capital Cost (EUR x 10^6)	Operating Cost (EUR/tonne)
1993	Bio	87	3000	O	In bio plant	In bio plant
1996	DAF	80	1200	O	0.4	130
1992	Bio	90	–	O	In effluent treatment plant	In effluent treatment plant

Table AIII.8 Equipment to Reduce Emissions to Air from Effluent Treatment Units

Facility	Year Built	Emission Controlled	Estimated % Reduction	Capital Cost (EUR x 10^6)	Operating Cost (EUR/tonne)
VOC Recovery (API ?)	1997	VOC odours	–	4.2	740
HC Recovery (Rotating Oil Drum Skimmer)	1983	VOC	50%*	0.6	–
API Separator Cover	1996	VOC	95%		–
API Separator	1988	VOC	20%	0.0	–
SWS Offgas to Incinerator	1993	H_2S, NH_3	–	1.3	112

best available techniques to reduce emissions from refineries - waste

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ABSTRACT

This report is one of a series prepared by CONCAWE on the available techniques for environmental protection in the oil refining industry. It describes a range of techniques utilised to manage wastes in oil refineries and in particular describes measures to minimise the quantities of wastes requiring disposal. It is intended to be part of the input for the development of BAT Reference Documents (BATREF) required under the Integrated Pollution Prevention & Control (IPPC) Directive.

KEYWORDS

Air emissions, BAT, best available technology, BREF, cost, effluents, emissions, groundwater, IPPC, oil, pollution, refinery, sludges, soil contamination, treatment, wastes, waste water, water

NOTE
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This report does not necessarily represent the views of any company participating in CONCAWE.

CONTENTS

IV.1. INTRODUCTION

This document is one section of a combined report prepared by CONCAWE on the available technologies for environmental protection in the oil refining industry. It is intended to be part of the input for the development of BAT Reference Documents (BATREF) required under the Integrated Pollution Prevention & Control (IPPC) Directive. [1] The report is mainly drawn from previous CONCAWE reports on waste minimisation in the industry [2] and on waste management in refineries . [3]

An important point is that there is no such thing as a universal “BAT”. Oil refineries differ in their size, complexity, the types of processes they operate, and the types of crude they process. By its nature, although the definition of BAT includes techniques as well as technology, it tends to concentrate on ‘end of pipe’ treatment. However, the use of appropriate techniques upstream to reduce either or both of the quantity of waste (including water) streams and the concentration of pollutants in them, can have significant effects in reducing the final quantities of wastes requiring disposal.

IV.1.1. DEFINITION OF WASTE

In the context of this report, waste is defined as any material to be disposed of, as being of no further primary use to the producer, but excluding aqueous and gaseous effluents from operating units.

IV.1.2. WASTE GENERATION

The generation of waste is an inevitable consequence of the operation of refineries. Such waste substances fall into two main categories:

(a) Non-hazardous waste, e.g. scrap metal and “domestic” wastes.

(b) Hazardous waste, e.g. sludges with a high lead content.

A definition of the term "hazardous" should be sought from national control authorities. Over-classification is definitely undesirable. In terms of the EU categorisation of wastes, most will now fall into category (b). A list of typical oil industry wastes is given in **Appendix IV.1**.

The report covers only wastes arising directly from industrial activities. Domestic type refuse, e.g. waste paper, is not included, being handled in the normal way by contract with local authorities.

Waste production in refineries represents a high operating cost and potential environmental risk, and as such its minimisation should be a priority.

IV.2. TECHNIQUES USED IN REFINERIES FOR WASTE MINIMISATION

For the purposes of this report, waste minimisation is defined as the reduction, to the extent economically feasible, of waste that is generated within a refinery and has subsequently to be disposed of. This definition is taken from a United States EPA report. [4]

Waste minimisation includes the following key elements:

IV.2.1. REDUCTION AT SOURCE

IV.2.1.1. Choice of Process

At the project and design stage of equipment or process, attention should be paid to the waste generation aspect. The choice of clean technology is to be preferred, e.g.:

- *Hydrogen Sulphide (H_2S)/Mercaptan (RSH) removal from process streams*:

  Traditional caustic washing produces spent caustic.
  Selective removal of H_2S with amines (regenerable process) and improved contactor design can minimise spent caustic production.

- *Cascading of Caustic Solutions*:

  An overall reduction in the caustic consumption of wet treating units can be obtained if semi-spent caustic from one treating unit can be re-used in another one. A typical example of this procedure is the use of the bleed of regenerated caustic (e.g. in Merox treaters for cat cracked gasoline or for removal of H_2S or thiophenols) in a pre-wash step of non-catalysed cat cracked gasoline sweetening processes. An example of a caustic integration scheme is given in **Appendix IV.2**.

IV.2.1.2. Process / Equipment Modifications

In a number of cases, relatively minor modifications can result in appreciable waste minimisation, e.g.:

- Installing mixers on crude oil storage tanks reduces sludge formation
- Closed loop sampling systems on product tanks reduces waste/slop oil production
- Re-sizing/improving condensate knock out system on gas streams & on-site recycle
- Mechanical seals on pumps
- Use of antifoulants/corrosion inhibitors
- Dissolved air flotation (DAF) units: use of polyelectrolyte instead of inorganic flocculants to reduce the mass for final disposal (e.g. by incineration or redistillation)

IV.2.1.3. Alternative Treatments

At times, the use of alternative treatments may result in either reduction or elimination of waste generation, or reduce the toxicity of the waste, e.g.:

- Hydrotreating instead of copper chloride sweetening
- Regenerative rather than once-through process (e.g. Merox process instead of caustic treatment)
- Hydrotreatment of lube products rather than acid treatment.

IV.2.2. RECYCLING OF WASTES

IV.2.2.1. Recycle / Reuse Within the Company

Recycling and reuse of wastes minimises the quantity for disposal. This applies mainly to oily wastes although other materials are now being recycled. Strict segregation is required and the correct choice of the dosing point is important. The effect of contaminants e.g. lead on catalysts or halides (organic chlorides) in waste etc. must be considered.

Examples:

- Reprocessing off-spec products
- Recovered oil as "synthetic feedstock" (e.g. oil from interceptor)
- Waste lubes as fuel component (depending on local regulations)
- Oily emulsions processed by a distillation column (e.g. from DAF unit)
- Use of spent caustic instead of fresh caustic for corrosion control on distillation unit.

IV.2.2.2. Recycle / Reuse Outside the Company

This will also minimise the quantities for disposal. Care must be taken to ensure that the material is handled responsibly and in an environmentally acceptable manner.

Examples:

- Some catalysts for metal recovery (reforming, desulphurisation)
- Waste lubes: re-refining
- Drums/containers: reconditioning
- Spent caustic can be used:
  - ⇒ in the paper industry
  - ⇒ for production of Na_2S or Na_2CO_3 and cresylic acids

- Alkylation process: CaF_2
  - ⇒ for HF production
  - ⇒ as a fluxing agent (steel industry)
- Resale of polymerisation plant catalyst as a fertiliser
- Sale of gypsum or sulphuric acid from flue gas desulphurisation units
- Paper, wood, glass, scrap metal
- Construction/demolition debris:
  - ⇒ concrete to a crusher, for use in road building etc.
  - ⇒ asphalt scrapings reused, e.g. in road building

IV.2.3. ECONOMY OF USE

Good plant operation and economy in the use of chemicals etc. will result in minimisation of wastes for disposal, e.g.:

- Correct conditioning of a catalyst during a run extends catalytic life
- Control of sodium content in visbreaker feedstock reduces coke formation
- Process optimisation leads to less off-specification product and hence less recycle
- Recycling caustic sufficiently can ensure it is completely spent (see **Appendix IV.2.**)

IV.2.4. HOUSEKEEPING

Good housekeeping is essential to waste minimisation. Seemingly unimportant procedural aspects in operations and maintenance may have a large impact on waste operations. A closer analysis of how certain waste streams arise, will in some circumstances allow complete elimination or at least reduction of the waste stream in a relatively inexpensive way.

Proper material handling and storage minimises the possibility of spills, leaks and other losses which result in waste. Examples of proper storage and handling include:

- Storage of drums off the floor to prevent corrosion through spills or concrete 'sweating'
- Keeping containers closed except when removing material
- Bunding of storage/process area to contain spills, with controlled drainage to a collection system e.g. interceptor
- Using larger containers instead of drums. Larger containers are reusable when equipped for top and bottom discharge, whereas drums have to be recycled or disposed of as waste

Spills and leaks generate waste. The best way to minimise this waste is to prevent spills and leaks occurring. Elements of a spill and leak prevention programme could be:

- Equipping storage tanks with overflow alarms and automatic pump shut-offs
- Installing double bottoms with integrated leak detection systems on tanks where practicable
- Using (double) mechanical seals on pumps
- Installing valves designed to minimise leakage.

When there is a risk of leaks or spills, the soil or floor should be rendered impermeable, and a collection system provided.

Cleaning, by its nature, generates waste. By choosing the right procedure and technique this waste may be minimised or its nature altered so as to make it more easily disposable:

- Drain equipment to the maximum
- Recycle "spent" rinse water
- Use high pressure water cleaning rather than detergents or chemicals
- Use on-site pre-treatment whenever possible, e.g. wash/steam filter material (e.g. filter clays) prior to dumping
- Minimise tank sludge prior to cleaning (solvent & mixers)

IV.2.5. WASTE HANDLING

Waste handling, when correctly done, optimises the economics and the ecological impact of the final disposal.

- Segregation of different wastes is a first priority. Addition of a small quantity of hazardous waste may turn a large quantity of inert waste into a problem
- Waste (pre) treatment often can make the choice of final disposal easier or more economical. Treatment is preferably carried out on site, to reduce the risk of spills or accidents during transportation

IV.2.5.1. Techniques

Sorting waste mixes e.g. concrete and scrap metal

- Could be cost-attractive (cheaper disposal routes for some components)
- Eliminates risk of unwanted components

Volume reduction

- De-oiling/dewatering of sludges gives small volume of solid, low solvent waste, (centrifuging or filtration)
- Asbestos lagging: special equipment for compaction & packing

Treatment to make waste environmentally more acceptable

- TEL/TML scale & sludge: permanganate treatment eliminates TEL/TML traces
- Oiled solids (soil): de-oiling in an oil extractor.
- Neutralisation: mixing polymerisation catalyst (H_3PO_4) with lime
- Process treatment by steaming, flushing or regeneration prior to disposal: clay and sand filters; catalysts

IV.2.6. HANDLING OF SPENT CAUSTIC SOLUTIONS

In refineries, caustic is universally used and spent caustic presents special problems and opportunities for minimisation as follows:

Minimisation of spent caustic generation

- Use of DEA or similar amine solution (regenerable)
- High efficiency contacting systems rather than a simple washing, optimising usage and so reducing quantity

Reuse within refinery

- Corrosion control on crude distillation units using spent caustic rather than fresh caustic
- Addition to biotreaters for pH control

Reuse outside refinery

- In paper mills (sulphidic caustic only)
- As raw material for Na_2SO_3, cresylics and Na_2CO_3 (may require segregation of sulphidic, cresylic and naphthenic caustics).

Disposal via the effluent system

- pH adjustment and pre-treatment maybe required.
- This might entail:
  - ⇒ oxidation to convert sulphides to thiosulphates
  - ⇒ acidification/stripping/extraction to allow removal of H_2S and organic acids
  - ⇒ neutralisation

IV.3. STORAGE

Wastes awaiting disposal must be stored in an environmentally acceptable manner, as approved by the local control authority. Storage must not give rise to secondary environmental problems such as odour or pollution of groundwater due to rainwater percolation through or run-off from the site. Storage should best be in closed vessels, containers or bags, on a site surrounded by a bund wall or toe wall, with drainage to a prepared system.

Special precautions are of course required for pyrophoric materials to eliminate the risk of fires; they must be kept wet, sealed or blanketed with inert gas.

IV.4. WASTE PRETREATMENT

IV.4.1. DEOILING/DEWATERING OF SLUDGES

Dewatering/deoiling is used to decrease the quantity of sludges for disposal and to recover oil from them. This topic is covered in **Section III** of this report covering emissions to water.

IV.4.2. SOLIDIFICATION, STABILIZATION AND ENCAPSULATION

Stabilisation and solidification are treatment processes designed to improve waste handling and physical characteristics, decrease surface area across which pollutants can leach, or limit the solubility of hazardous constituents. The following definitions are commonly used:

Solidification – A process in which materials are added to the waste to produce a solid. It may involve a solidifying agent that physically surrounds the contaminant (i.e. cement or lime), or it may utilise a chemical fixation process (i.e. sorbents). The resulting waste is usually an easily handled solid with low leachability.

Stabilisation – The conversion of a waste to a chemically stable form that resists leaching. This may be accomplished by a pH adjustment. Stabilisation also generally results in a solidification of some sort (monolith or dry granular solid).

Encapsulation – Complete coating or enclosure of a waste with a new, non-permeable substance.

IV.4.2.1. Cement-based Processes

In this process the slurried waste is mixed with cement and during the hardening process is incorporated in the rigid concrete matrices.

The process is especially effective when the waste contains metals because at the high pH of the cement mixture most metal compounds are converted into insoluble metal hydroxides. In the case of spent catalyst, most metal compounds are present as hydroxides which as such may also increase the strength and stability of the waste containing concrete. On the other hand, the presence of organic impurities may act as interfering agents to the curing of the concrete and this limits the application of this disposal route.

IV.4.2.2. Reuse of Spent FCCU Catalyst as Feed to the Cement Industry

Spent catalytic cracker unit (FCCU) catalyst may be used as an additive in cement manufacturing. When the cement is used, the catalyst component forms insoluble hydrates with the chalk present in the cement mixture, which also gives beneficial fixation of heavy metals.

IV.4.2.3. Chemical Stabilisation

These processes are based on the reaction of lime with waste materials and water to form a chemically stable product. This technique is suitable to immobilise watery sludges to yield a powdery hydrophobic product which can be compacted. The immobilised product, is water-repellent and hardens with time and often has very good properties for civil engineering applications like foundations, tank bases, bundwall and road making.

When compacted, the porosity to water is very low. This reduces the risk of leaching.

IV.4.2.4. Micro-encapsulation and Macro-encapsulation

The micro-encapsulation techniques are based on the reduction to surface-to-volume ratio of the waste by formation of monolithic, hard mass with a very low permeability. Macro-encapsulation is the enclosing of a relatively large quantity of waste, such as an entire waste container. Wastes are macro-encapsulated by surrounding them with a stiff, weight-supporting matrix, and a seam-free jacket.

Encapsulation is suitable for on-site treatment of disposal sites of accumulated spent acid tars and oily sludges which are difficult to transport and to dispose of by other means. A disadvantage is that the treated product occupies a larger volume than the original sludge.

Because it can be applied on-site, the encapsulation process may be considered for single applications like rehabilitating refinery sites after decommissioning or cleaning up an oil-polluted site after a spill. The decision to apply the process depends on the future use of the site and local legislation. The process is less attractive for the treatment of regularly produced sludges, because of the increased mass generated for disposal.

IV.4.2.5. Thermoplastic Techniques

In general the use of thermoplastic solidification techniques is restricted to dry solid materials. This technique should not be used for wastes, containing:

Organic chemicals (these may act as solvents).

Oxidising salts (these can react with the organic material causing deterioration to the matrix material; at elevated temperatures these mixtures are extremely flammable).

Dehydrated salts (e.g. sodium sulphate easily dehydrates at temperatures required to plasticise bitumen; when the bitumen matrix is soaked in water, rehydration of the sodium sulphate can occur, and this can cause the bitumen to swell and split apart).

The processing of waste with bitumen is applied in the oil manufacturing industry as a disposal method for spent FCCU catalyst and used for the production of a filler component in road asphalt where the catalyst is present as a minor component. The catalyst particles are completely encapsulated which makes aqueous extraction unlikely.

IV.4.2.6. Mixing with Asphalt

This process allows treatment of soils with high levels (up to 10%) of high boiling range hydrocarbons. The soil is mixed with asphalt to produce a stable end product suitable for use in road construction.

IV.5. WASTE DISPOSAL METHODS

All disposal must be carried out at suitability authorised and assessed facilities in accordance with the conditions laid down by the local control authority. In the event that incineration, recovery or reprocessing are involved, local company management should be satisfied that secondary waste generated by these processes is also disposed of at suitably authorised sites.

IV.5.1. DISPOSAL ROUTES

IV.5.1.1. Landfill

The deposition of wastes on to land as a method of disposal will always be an activity which is controlled under legislation. In some countries it remains one of the cheaper methods of disposal although the shortage of satisfactory sites and the difficulties in obtaining licences from the regulatory authorities is driving prices higher.

The key consideration in the operation of a landfill site is the protection of groundwater from contamination by the materials contained in the landfill. It is therefore essential that:

- The lining of the containment is impermeable. Clay is the preferred material in many parts of Europe. In others, a lining of plastic sheeting is used. The integrity of synthetic liners is open to some doubt. In some countries it is required to have multi-layer linings with integrated drainage systems for new landfills.
- Monitoring boreholes are used in order to inspect the effectiveness of the containment.
- The deposition of liquid wastes is not permitted except under rigorously controlled conditions. Whether or not liquid deposition is allowed, arrangements should be made for the collection and treatment of leachate.

The second consideration for the disposer is that wastes deposited in landfill are not immediately destroyed but only stored. They must not be capable or reacting in a harmful way to generate heat or noxious gases. If flammable gases e.g. methane are generated, they should be collected. It is important to minimise the risk of any future liability. The producer should therefore operate the site himself, in which case he will then retain responsibility for his own waste, or select a disposal site operator who will operate in a safe, reliable, and environmentally responsible manner (see **Section IV.5.3**).

IV.5.1.2. Underground Storage

One of the disposal routes which is used for hazardous materials is the underground storage in worked-out salt mines and caverns, or by deep injection. However, there are no reports available which confirm that this type of underground storage is being used for refinery waste in Western Europe.

The materials being disposed in this way are reportedly:

- Persistent chemical waste
- Dioxin containing sludges (from dump site leachate treatment)
- Nuclear waste
- Other hazardous materials

Various types of underground storages have been used, or proposed in different parts of the world. These are:

- Deposition in old excavated salt mines
- Deposition in used brine wells
- Injection into deep rock strata
- As with landfill deposition, the key factor is the risk of groundwater contamination. The principal considerations associated with this are:
- The mechanisms by which contaminant migration can be prevented
- The methods available to detect contaminant migration if it should occur
- Possible remedial actions

Deep deposition precludes any real possibility of effective monitoring or remedial action. The integrity of the system depends therefore on the certainty that contaminant migration will not occur. Such certainty, in turn, depends on a comprehensive knowledge of the surrounding geology and on the assurance that no faults or fissures are present.

The choice of disposal route obviously depends on local records and on the nature of the waste to be disposed of.

Sedimentary deposits of salt will not usually present an irregular geological structure, but the use of disused salt mines or brine wells is limited to dry wastes or water insoluble wastes for obvious reasons.

Injection into deep rock and clay strata has been considered for wastes from the nuclear industry, and is used for some oil industry wastes.

IV.5.1.3. Incineration

Any process that uses combustion to convert a waste to a less bulky, less toxic or less noxious material is called incineration.

An incineration system must produce as complete combustion as practical using an optimum selection of governing parameters (time, temperature and turbulence) and provide air pollution control devices to minimise the emission of air pollutants. Many waste materials are readily combustible and the products of their combustion are harmless gases which are easily disposed of through vents or stacks to the atmosphere. In such cases, incineration is often the soundest method of waste disposal.

Some of the factors that characterise incinerators with good performance are given below:

- Complete combustion
- Adequate flue gas treatment
- Clear stack
- Low maintenance
- Minimum materials handling
- Minimum operating labour
- Adequate capacity
- Adequate availability

IV.5.1.4. Types of Incinerators

Fixed Hearth Incinerators

In its simplest form, a fixed hearth incinerator is a refractory lined chamber into which solid or sludge waste is introduced through a side port. Waste accumulates on the hearth where it is ignited and burned to ash.

Because the solids, sludges and high viscosity liquids will not be mixed thoroughly with combustion air in a fixed hearth, a provision must be made to enhance destruction of all organics by adjusting the rates of waste introduction and ash removal.

Experience has shown that maintenance costs are low because there are few internal moving parts. Because this type of incinerator can be constructed in small sizes, it is frequently employed for batchwise destruction of small quantities of waste at the site of generation. It is not usually applied to destroying large volumes of wastes and it is not often used in refineries. These incinerators can handle wastes such as oil spill debris or contaminated soils, activated carbon, plastic, resins, desiccants, sorbents, asphalt, wood and paper.

Multiple Hearth Incinerators

The multiple hearth incinerators are capable of handling high volume of waste and may use supplementary fuel. The incineration chamber is almost always a vertical steel cylinder, lined with refractory. A number of horizontal platforms are located at various levels in the chamber and the top platform usually receives a continuous charge of waste material.

Multiple hearth incinerators are best suited to wastes with a high water content and of a uniform particle size (sludge).

Maintenance is high because of internal moving parts. Capital costs are high and multiple hearth technology has very limited applications in refineries.

Fluidised Bed Incinerators

In a fluidised bed incinerator, the sludge is pumped into a hot fluidised bed of special sand about 1-3 mm mean diameter. This ensures that any material volatilised is combusted.

The fluidised bed incinerator is used to burn sludges partially dewatered and pumped to the unit with a solids content of up to 5-6% wt. If support fuel is required refinery gas can be used.

Air for combustion and fluidisation is provided by a compressor and is pre-heated before passing into the incinerator bed.

The main advantage of this type of incinerator is its flexibility to accommodate large variations in sludge composition.

Rotary Kiln Incinerators

The rotary kiln incinerators are considered the most versatile and most durable of the common incinerator types. They can incinerate almost any waste, regardless of sizes and composition. A rotary kiln incinerator is a refractory lined cylindrical steel shell slightly tilted on its horizontal axis. The shell is usually supported on two or more heavy steel tracks which band the shell. These ride on rollers allowing the kiln to rotate around its horizontal axis. Waste material is "tumbled" through the kiln by gravity as it rotates. The rate of rotation and horizontal angle to tilt determines the amount of time the waste is held in the kiln (solids residence time). Rotary kilns can receive solid waste through one end which is non-rotating by means of an auger screw or ram feeder. Pumpable, non-dispersible waste and sludges may be introduced through a water cooler tube and liquid waste may be injected into the kiln through a burner nozzle. As with a liquid injection incinerator, auxiliary fuel can be fired into the kiln chamber. Combustion air can be introduced in a variety of ways to enhance turbulence in the kiln chamber.

Kilns often have secondary combustion chambers and usually are equipped with air pollution control. Because of its versatility and durability, a rotary kiln can treat virtually any hazardous waste, including drums and packaged wastes.

Appendix IV.3 provides some general guidance on the types of incinerators for combusting industrial wastes.

Liquid Fuel Incinerators

A liquid waste fuel must be changed to gas to burn and this requires that waste must be pumpable and atomisable (dispersible into very small droplets). The waste is delivered to the incinerator by a conventional pumping system and passes through a burner into the incinerator chamber.

Gas or Fume Incinerator

These are incinerators which burn only gas or volatilised material (fumes). They are very similar to liquid injection types except that the fluid is gas instead of a liquid.

IV.5.1.5. Pyrolysis

Pyrolysis is a thermal conversion of solid wastes, biomass etc. generating quantities of a high calorific value gas which can be burned further in a furnace or in an incinerator. This process is not applied in refineries for waste and sludge treatment because incineration is simpler and is preferred.

IV.5.1.6. Biodegradation Methods

Many hazardous chemicals present in refinery waste can be converted by microbiological methods to harmless compounds such as water and carbon dioxide.

In general, the microbiological degradation of contaminants in soil is very slow in nature, because process conditions for such degradation are seldom favourable. To accelerate degradation a number of conditions have to be fulfilled. The most important factors are the availability of temperature control, sufficient oxygen, nutrients, and the appropriate micro-organisms. Also important are the concentration level of the contaminants and the variation in concentration. The presence of toxic compounds can disturb the degradation process. Sometimes the presence of natural organic compounds has a positive influence on the biodegradation process.

Current techniques for biological decontamination are based on optimisation of the process conditions for microbiological degradation. The appropriate micro-organisms for microbiological degradation may already be present in the soil to be treated or may have to be added. The latter is necessary if special micro-organisms are required. These special micro-organisms can be obtained by selection and adaptation.

In summary the following conditions have to be met in order to optimise the degradation rate:

- Sufficient number of micro-organisms of the right strains
- Non-toxic concentrations of contaminants of other compounds
- Presence of sufficient water (10-15% wt in soil)
- Presence of sufficient nutrients (mainly P and N in ratio 1:10)
- Presence of sufficient oxygen for aerobic processes and a full depletion of oxygen for anaerobic processes
- Favourable temperature (10-30°C)
- Sufficient availability of contaminants (preferably without high peak concentrations) to the micro-organisms
- Soil of pH 6-8
- temperature control.

Several types of techniques are possible for the micro-biological treatment of contaminated soil.

Landfarming

Landfarming systems have been used for the treatment of petroleum industry wastes for many years. The process involves the controlled application of waste on a soil surface in order to biodegrade the carbonaceous constituents by utilising the micro-organisms that are naturally present in the soil. The conditions under which the degradation takes place are typically aerobic.

Landfarming should not be confused with land filling, in which the waste is deposited in man-made or natural excavations for an indefinite period of time. The conditions under which land-filled wastes are stored are typically anaerobic.

In most locations permission from the authorities is required before a landfarming facility can be started. In a number of countries the technique is not permitted at all.

The advantages of landfarming are that it is a relatively cost-effective and simple technique, which is environmentally acceptable provided that it is properly designed, operated and monitored (particularly with respect to leachate and run-off).

Composting

In composting techniques, enforced aeration of the soil takes place. These techniques are, to a very large extent, similar to the open and closed composting systems, already used in practice for treating organic wastes. Some adaptation is necessary, due to the fact that the mechanical/physical behaviour of soil is different from that of organic wastes. Also for these techniques treatment periods of one to two years may be necessary.

However, experience with commercially available bio-treatment processes with oil contaminated soil in contained areas with controlled climate (in housings) shows that the degradation process can be accelerated to a few months or even few weeks.

Biopiling

Biopiling is an adaptation of the landfarming and composting techniques. Oily sludge is mixed with soil (as a source of bacteria), treated with a pre-determined amount of nutrients, and maintained in a controlled climatic environment under optimum conditions of temperature, air and moisture levels. Biodegradation proceeds rapidly, and (with control authority agreement) the end product is suitable for use as cover material on completed waste tips or in landscaping areas.

Biopiles may vary from highly engineered commercial facilities to minimally engineered temporary ones such as tarpaulin covered soil/sludge piles.

Mechanised Processes

The third category consists of the wet and dry bioreactors and/or fermenters in which the soil is continuously mixed intensively.

The biological composting/decontamination process can be more accelerated if the necessary process conditions are closely controlled and monitored. This is not possible in housings but can be achieved in vessels, which are vacuum and pressure tight.

There are bioreactors and fermenters designed, manufactured and already in commercial operation which meet the following conditions:

- Capacity: up to 200 tons for a single charge
- Vacuum or pressure operation
- Humidity control
- Operation under aerobic or anaerobic conditions
- Mechanical stirring of the entire charge
- Residence time between few hours and few days depending on type and grade of contamination. Typical hydrocarbons need a few hours to degrade (whereas PCBs require several days).

IV.5.1.7. Disposal of Spent Catalysts

Refinery catalysts typically consist of metals supported on an inert carrier such as alumina, silica or activated charcoal. The metals may be precious, such as platinum or rhenium in a reformer catalyst, or heavy base metal elements such as nickel, molybdenum, cobalt, tungsten, and vanadium e.g. nickel-molybdenum for a hydrotreater catalyst. Sometimes non-metal catalysts are used such as phosphoric acid in the catalytic polymerisation process.

In use, the catalysts become contaminated with metals such as lead, arsenic, nickel and vanadium, non metals like sulphur and carbon, and significant quantities of hydrocarbon products and residues.

In view of the metals value, spent catalysts containing precious metals are returned to the manufacturers for regeneration, whilst others are sent for metals reclamation and recycling. Other industries can also use spent catalysts in the manufacture of other products: e.g. those containing nickel, cobalt and molybdenum can be used in the production of ceramic tiles. Waste catalyst can also be combined with waste products from other industries to make useful products: e.g. catalysts containing phosphoric acid can be mixed with aluminium industry waste alkali mud to make a soil amendment product. Spent catalysts containing metals can also be used as a component in cement manufacture or be combined with asphalt as a road base.

Those catalysts which contain activated charcoal, or are highly contaminated with hydrocarbon residues, have a calorific value which can be used as fuel in e.g. cement manufacture.

Those catalysts which cannot be recycled/reclaimed have to be disposed of by other approved routes such as e.g. landfill.

IV.5.2. CO-MINGLING OF WASTE

In some countries the co-mingling of non-hazardous wastes with hazardous materials from elsewhere (and vice versa) is not permitted, while in others, this is a recognised and accepted means of disposal. The microbial organisms generated in the non hazardous wastes can destroy the toxic elements in the hazardous waste.

In any event, the location of a company's wastes within a disposal site should be ascertained. In addition, the number of disposal sites utilised should be minimised. It is not good practice to "spread the waste around".

IV.5.3. SELECTION OF WASTE DISPOSAL ROUTE, SITE AND CARRIER

The aim of this section is to recommend, in simple practical terms, the way in which the above should be selected. It starts from the point at which a company has considered how to minimise the environmental impact of a particular industrial activity and has concluded that the best practicable environmental option entails the consignment of a particular solid or liquid waste to landfill, biodegradation or incineration.

It is recommended that the following steps are taken to ensure that "Duty of Care" is adequately fulfilled.

STEP 1 - Identification of Suitable Waste Disposal Sites

Determine the hazard characteristics of the waste and whether or not it requires special treatment.

Determine the optimum batch size for disposal and the frequency of arising of the waste.

In conjunction with the local waste disposal authority, identify the disposal methods likely to be acceptable and the sites appropriately authorised to receive such waste.

For each waste disposal site to be considered:

- Obtain a copy of the relevant waste disposal licence (or authorisation)
- Check the technical and financial standing of the operating company and its insurance cover

STEP 2 - Assessment of Disposal Site Management and Operation

Before selection, the proposed disposal site should be visited by an assessment team, normally consisting of at least two persons who have between them, intimate knowledge of the variability of the waste in question and general experience of the method of waste disposal proposed.

Consider the following questions:

All Disposal Sites

(1) Are operatives aware of the disposal principles applying?

(2) Is there a responsible attitude to acceptance and treatment of wastes?

(3) Are all loads weighed into the site?

(4) Are full records kept of all loads received?

(5) Is there adequate segregation of waste types?

(6) Is the site secure against intruders?

(7) Does the site have a good safety record?

(8) Is the housekeeping good?

(9) Is the site a source of neighbourhood nuisance?

(10) Do vehicles leave with dirty tyres?

(11) Are there written operating procedures?

(12) Are there written emergency procedures?

(13) Are there adequate fire fighting facilities?

(14) Are safety and environment protection facilities adequate?

Landfill and Biodegradation Sites

(15) Is there a rational plan for site utilisation?

(16) Are there records of placings of all hazardous loads?

(17) Is all water run-off controlled and adequately treated?

(18) Is there adequate protection against groundwater contamination?

(19) Is there any provision for laboratory testing of wastes, groundwater and leachates?

Incineration Sites Only

(20) Is there a smoke or other fume problem?

(21) Is the stack particulates removal adequate?

(22) Are records of incinerator temperature available?

(23) Is the process temperature control reliable?

(24) Is site drainage disposed of correctly?

(25) Are incinerator ash and other site wastes disposed of correctly by an acceptable route?

(26) What assurance is there that wastes for incineration are properly incinerated?

(27) Is any waste pre-treatment performed in an acceptable manner?

In addition to these checks, the suitability of the site for the waste in question should be discussed with the waste disposal authority responsible for the site.

If any doubt remains over the adequacy of the site for collection and disposal of leachate waters from the wastes, discuss this matter with the water control authority responsible for the area.

If any doubt remains over possible neighbourhood nuisance from an incinerator used to burn waste, discuss this matter with the air pollution control authority.

STEP 3 - Selection and Assessment of a Waste Carrier

Having selected a waste disposal site and determined the waste production rate, a waste carrier must be selected who can be relied upon to transport the waste safely, cleanly and efficiently from the company's site to the waste disposal site. Waste carriers not used previously should be assessed by company representatives experienced in the employment of waste contractors.

Consider the following questions:

(1) Do the proposed carriers have experience of carrying the types of waste in question and of waste disposal site operations?

(2) Do they keep good records of waste loads carried?

(3) Do they have equipment suitable for handling the waste in question?

(4) Do they have equipment suitable for operation within petroleum sites?

(5) Are operatives provided with appropriate protective equipment?

(6) Have there been any convictions for waste disposal offences?

(7) Is any special insurance carried for risks associated with waste handling?

(8) Do they know how to react to spillages and do they carry equipment/ protection to deal with spillages?

Contact for "references", the waste disposal authority within whose area the carrier's business is registered.

STEP 4 - Follow-up

Keep good records of the quantities and compositions of all waste consignments dispatched to disposal sites.

Make periodic audit visits to the waste disposal site to assess ongoing acceptability of the disposal methods employed. Record observations made during these visits.

In the case of hazardous wastes, keep and update a plan of the waste disposal site marked up to show the area in which waste has been placed in case of future liability.

IV.6. DOCUMENTATION AND LABELLING OF WASTES

IV.6.1. DOCUMENTATION

All waste moved from oil company sites to disposal sites must be accompanied by some type of waste transfer advice form, as agreed between the company site management and the local control authority. This is to ensure that:

- Control authority requirements are met; and
- Records are maintained of all waste movements from company sites.

Contact should be made with local authorities to ascertain their requirements. In the event that there are none, an "in-house" system should be established.

IV.6.2. LABELLING OF CARGOES

Wastes for disposal may be transported by road, rail, sea or even air, and in each case it is necessary to ensure that the consignment is labelled in accordance with national and international regulations. Since these will vary between countries and across national boundaries, requirements should be checked with local and national control authorities.

In any event, the minimum labelling that is required to fulfil a "duty of care" commitment is:

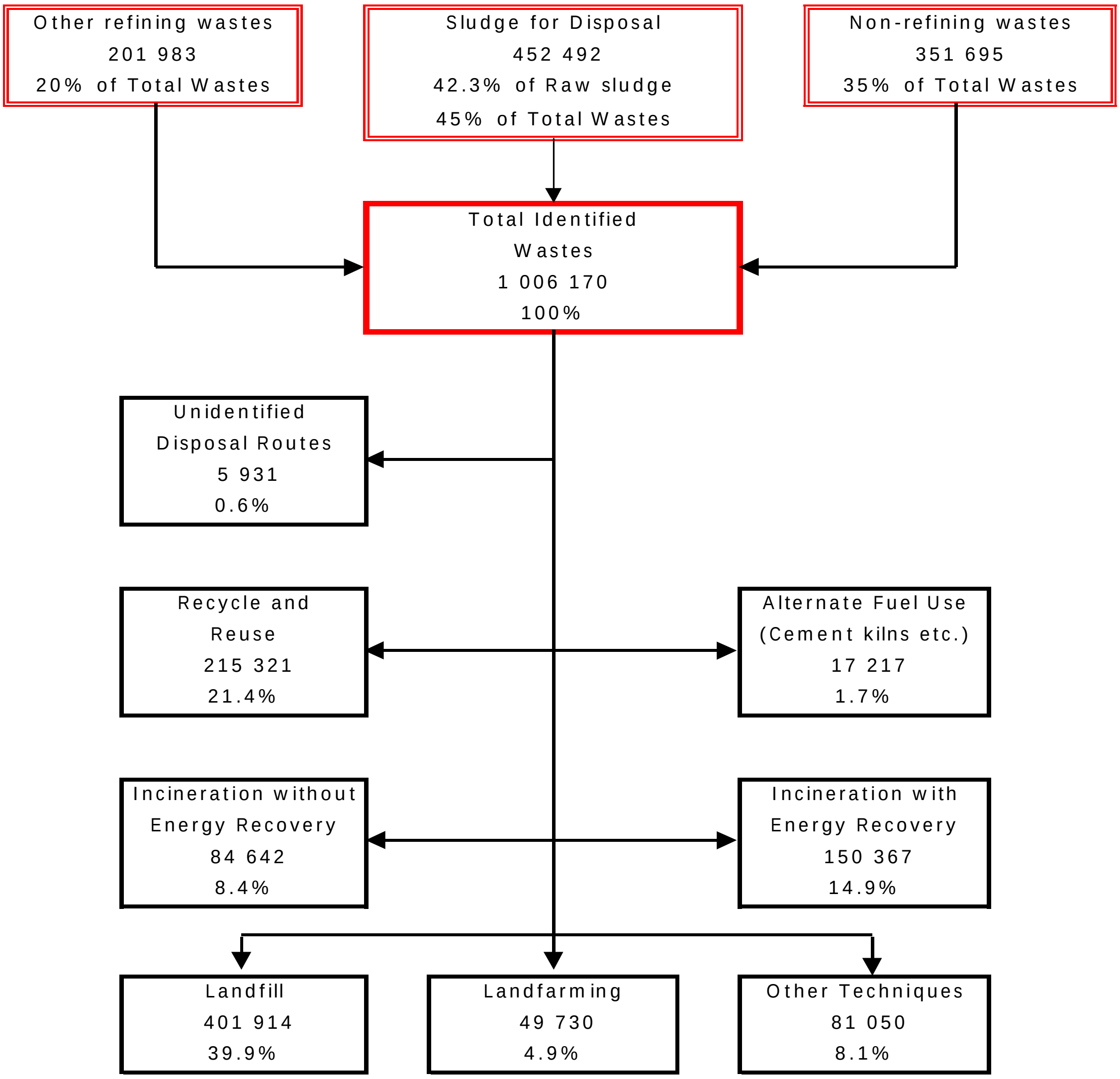
- The name of the waste
- The name, address and telephone number of the producer
- Any potential safety or environmental hazards (e.g. release of H_2S)
- Precautions and action required in the event of a spillage
- Flash point (if appropriate)
- Address and telephone/fax number for specialist advice

In some countries considerably more detail than this is required, and so it is most important that local regulations be consulted. Since these can change quite quickly, no attempt has been made to list them in this report.

IV.7. QUANTITIES

The quantities of wastes generated by European oil refineries (excluding sludge pretreatment) is summarised in **Figure IV.1** below. These data are taken from a CONCAWE survey for 1993. [3]

Figure IV.1 Summary of Total Waste Generation and Disposal Routes



All weights in tonnes

Non-refining wastes are those wastes which are not specific to oil refining

IV.7.1. OTHER REFINING WASTES

The total amount of identified other refining wastes consisting of those wastes, other than sludges, which are specific to the refining process (e.g. spent catalysts, tank scales, contaminated soils, etc.) produced in 1993 by the 89 European refineries reporting was 201 983 tonnes (i.e. 0.04% wt of the total refinery throughput).

The sources of these wastes and the disposal routes for them are listed in **Table IV.1** below.

Table IV.1 Generation and Disposal of Other Refining Wastes

Other Refining Wastes Production			**tonne/yr**
FCCU Catalyst			39 129
Reformer Catalyst			902
Desulphurisation Catalyst			6 368
Other Catalysts			9 486
Spent Clay			5 367
Sorbents			3 826
Tank Scales	Leaded		375
Tank Scales	Unleaded		4 387
Acid tar			483
Spent Caustic	(Where disposed of as waste)		12 074
Spent Chemicals			2 359
Flue Gas Desulphurisation			2 529
Contaminated Soil			53 136
Miscellaneous Oily Wastes			18 046
Other Wastes			31 336
Incinerator Ash	(Also included in sludges)		12 180
Total other refining wastes			201 983
Other Refining Wastes			**tonne/yr**
Total Identified Waste for disposal			201 983
Wastes to Identified Disposal Routes			200 526
Balance (Identified - Unidentified Disposal)			1 457
Waste Identified (% of Throughput)			0.04%
Total Identified Other Refining Waste to:		**% wt**	**tonne/yr**
Recycle/reuse		30.2	60 961
Landfill		43.6	88 001
Landfarm		5.2	10 588
Incineration with Energy Recovery		7.8	15 776
Incineration without Energy Recovery		4.2	8 500
Other Disposal Routes		8.3	16 700
Unidentified		0.7	1 457

IV.7.2. SPENT CAUSTIC SODA

The total quantity of spent caustic reported amounted to 190 295 tonnes. Where caustic soda is reused on site or disposed of through the effluent treatment system, it is not considered as a waste. The 12 094 tonnes reported in **Table IV.1** as spent caustic therefore represent that quantity which is disposed of off-site and clearly identified as a waste. The quantity of spent caustic which was reported as not disposed of as waste was 178 221 tonnes.

IV.7.3. NON-REFINING WASTES

This category includes those wastes which are not specific to oil refining such as construction, demolition and "domestic" wastes (e.g. kitchen, office etc.). These are listed in **Table IV.2** along with information on the disposal routes used and costs. The total quantity of these reported in 1993 by the 89 refineries reporting was 351 695 tonnes.

Table IV.2 Generation and Disposal of Non-refining Wastes

Construction / Demolition and Domestic Wastes		**tonne/yr**
Scrap Metal		50 224
Rubble		147 455
Domestic		154 016
Total		351 695
Construction / Demolition / Domestic Wastes		**tonne/yr**
Total Identified Waste for disposal		351 695
Wastes to Identified Disposal Routes		350 895
Balance (Identified - Unidentified Disposal)		800
Waste Identified (% of Throughput)		0.07%
Total Construction and Domestic Waste to:	**%wt**	**tonne/yr**
Recycle/reuse	43.9	154 360
Landfill	51.6	181 374
Landfarm	0.0	0
Incineration with Energy Recovery	2.4	8 550
Incineration without Energy Recovery	0.9	3 228
Other Disposal Routes	1.0	3 383
Unidentified	0.2	800

IV.8. DISPOSAL ROUTES USED BY REFINERIES

Many refineries use more than one method of disposal as appropriate for the properties of the various wastes produced. The disposal of wastes can take place both on-site and off-site.

The categories of waste (excluding sludges) for disposal from the 89 reporting Western European oil refineries were:

- 36.5 % other refining wastes
- 63.5 % non-refining wastes

This means that over half of the reported waste for disposal was not specific to oil refineries.

The total amount of these wastes for disposal was 554 000 tonnes, i.e. an average of 6 200 tonnes/year per refinery. Of this:

- 23.1% went to recycle, reuse and alternate fuel use off-site
- 23.3% was destroyed by incineration
- 4.9% was disposed of by landfarming
- 39.9% was sent to landfill
- 8.8% was treated by other techniques

The quantities of the various categories of wastes disposed of by the various routes are presented in **Table IV.3**.

Table IV.3 Waste Disposal Routes

Wastes Disposed by:	**Other Refining**	**Non-Refining**	**All Wastes**
Disposal Route (tonnes)			
Recycle/reuse	60 961	154 360	215 321
Landfill	88 001	181 374	269 375
Landfarm	10 588	0	10 588
Incineration with Energy Recovery	15 776	8 550	24 326
Incineration without Energy Recovery	8 500	3 228	11 728
Other Disposal Routes	16 700	3 383	20 083
Unidentified	1 457	800	2 257
Percentage to each Route (% wt)			
Recycle/reuse	30.2	43.9	38.9
Landfill	43.6	51.6	48.7
Landfarm	5.2	0.0	1.9
Incineration with Energy Recovery	7.8	2.4	4.4
Incineration without Energy Recovery	4.2	0.9	2.1
Other Disposal Routes	8.3	1.0	3.6
Unidentified	0.7	0.2	0.4

IV.9. WASTE DISPOSAL COSTS

In the survey of the costs of refinery waste disposal, cost data were reported for 415 000 tonnes or 75%. The total reported costs are summarised in **Table IV.4**.

For the 89 European refineries, the total reported cost was about 22 000 000 EUR.

Table IV.4 Costs of Waste Disposal Methods

Wastes Disposed by:	**Other Refining**	**Non-refining**	**All Wastes**
Total Reported Costs of: (EUR/year)			
Recycle/reuse	4 503 485	904 602	5 408 088
Landfill	7 010 488	3 576 907	10 587 395
Landfarm	114 183	none	114 183
Incineration with Energy Recovery	2 213 660	754 870	2 968 530
Incineration without Energy Recovery	1 377 379	160 893	1 538 271
Other Disposal Routes	1 016 813	222 346	1 239 159
Total	16 236 008	5 619 618	21 855 626
Average Costs of: (EUR/tonne)			
Recycle/reuse	89	10	37
Landfill	105	24	49
Landfarm	17	none	17
Incineration with Energy Recovery	156	88	131
Incineration without Energy Recovery	209	126	195
Other Disposal Routes	90	66	85
Overall	104	22	53

The cost of disposal includes transportation costs. In many cases these are a significant proportion of the total cost. From the returns where transportation and disposal costs were reported separately, an average transportation cost of 13 EUR/tonne was calculated.

IV.9.1. LANDFILL

The total reported cost of disposing of all wastes going to landfill was about 11 000 000, EUR yielding an average cost of 49 EUR/tonne. However, the cost of landfill varies widely around this average cost figure. This is depicted in **Table IV.5** where cost ranges are presented versus the different waste categories. This shows that most of the cheapest landfill disposal is for non-refining wastes. This information is some years out of date. A limited survey of more recent costs reported in the companion section on sludge disposal showed that the average waste disposal cost was some 50% higher in this survey than reported here. This probably reflects a real increase in costs due to the higher standards of waste disposal which have been introduced over recent years. However, it must be stressed that these data are based on a much smaller sample.

Table IV.5 Range of Costs for Disposal of Wastes by Landfill

Cost Range for Landfill (EUR/tonne)	Other Refining Wastes (tonnes)	Non-refining Wastes (tonnes)	Total Wastes (tonnes)
0 to 20	15160	67251	82411
20 to 45	11242	65353	76595
45 to 65	4482	5946	10428
65 to 85	9128	4089	13217
85 to 110	5881	2862	8743
110 to 130	2150	1948	4098
130 to 150	6695	729	7424
150 to 175	1338	21	1359
175 to 215	3015	0	3015
215 to 260	4079	119	4198
260 to 350	2574	250	2824
350 to 430	141	0	141
430 to 865	314	0	314
865 to 1700	1082	0	1082
>1700	21	0	21
Total	67301	148569	215870
Average (EUR/t)	105	24	49

IV.9.2. INCINERATION

The total reported cost for incineration was about 4 500 000 EUR. The average cost was 147 EUR/tonne. Again a wide spread of cost ranges for incineration was observed as shown in **Table IV.6**. Similar comments as to current costs can be made as in **Section IV.9.1** above.

Table IV.6 Range of Costs for Disposal of Wastes by Incineration

Cost Range for Incineration (EUR/tonne)	Other Refining Wastes (tonnes)	Non-refining Wastes (tonnes)	Total Wastes (tonnes)
0 to 20	2397	2248	4645
20 to 45	910	4661	5571
45 to 65	260	407	667
65 to 85	194	84	278
85 to 110	2382	0	2382
110 to 130	1275	2684	3960
130 to 150	1982	0	1982
150 to 175	1819	441	2260
175 to 215	5161	0	5161
215 to 260	3288	356	3644
260 to 350	289	0	289
350 to 430	1008	0	1008
430 to 865	486	0	486
865 to 1700	102	0	102
>1700	9	0	9
Total	21561	10881	32442
Average (EUR/t)	173	93	147

IV.9.3. RECYCLE AND REUSE

Total reported cost on recycle and reuse was more than 4 700 000 EUR. Again there was a wide range of costs with the average cost at 37 EUR/tonne. For catalysts and chemicals, this cost was higher at an average 90 EUR/tonne, while for non-refining waste, obviously this was much lower at 10 EUR/tonne. In fact scrap metal was often sold, i.e. disposal at a negative cost.

IV.9.4. OTHER TECHNIQUES

The reported cost for other disposal routes was about 1 000 000 EUR, or an average of 85 EUR/tonne.

IV.10. REFERENCES

1. EU (1996) Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. Official Journal of the European Communities No. L257, 10.10.1996

2. CONCAWE (1990) A field guide on reduction and disposal of waste from oil refineries and marketing installations. Report No. 5/90. Brussels: CONCAWE

3. CONCAWE (1995) Oil refinery waste disposal methods, quantities and costs - 1993 survey. Report No. 1/95. Brussels: CONCAWE

4. EPA (1988) Waste minimization opportunity assessment manual. Report No. 625/7-88/003. Washington DC: Environmental Protection Agency

APPENDIX IV.1 TYPICAL WASTE TYPES

Oiled materials

- *oily sludges*

  tank bottoms
  biotreatment sludges
  interceptor sludges
  waste water treatment sludges
  contaminated soils
  desalter sludges

- *solid materials*

  contaminated soils
  oil spill debris
  filter clay acid
  tar rags, filter materials, packing, lagging
  activated carbon

Drums and containers

metal
glass
plastic
paint

Non-oiled materials

- spent catalyst (excluding precious metals)

  FCCU (fluid bed catalytic cracking unit) catalyst
  hydrodesulphurisation / hydrotreatment) catalyst
  polymerisation unit catalyst
  residue conversion catalyst

- other materials

  resins
  boiler feed water sludges
  desiccants and absorbents
  neutral sludges from alkylation plants
  FGD wastes

Radioactive waste

catalysts
laboratory waste

Scales

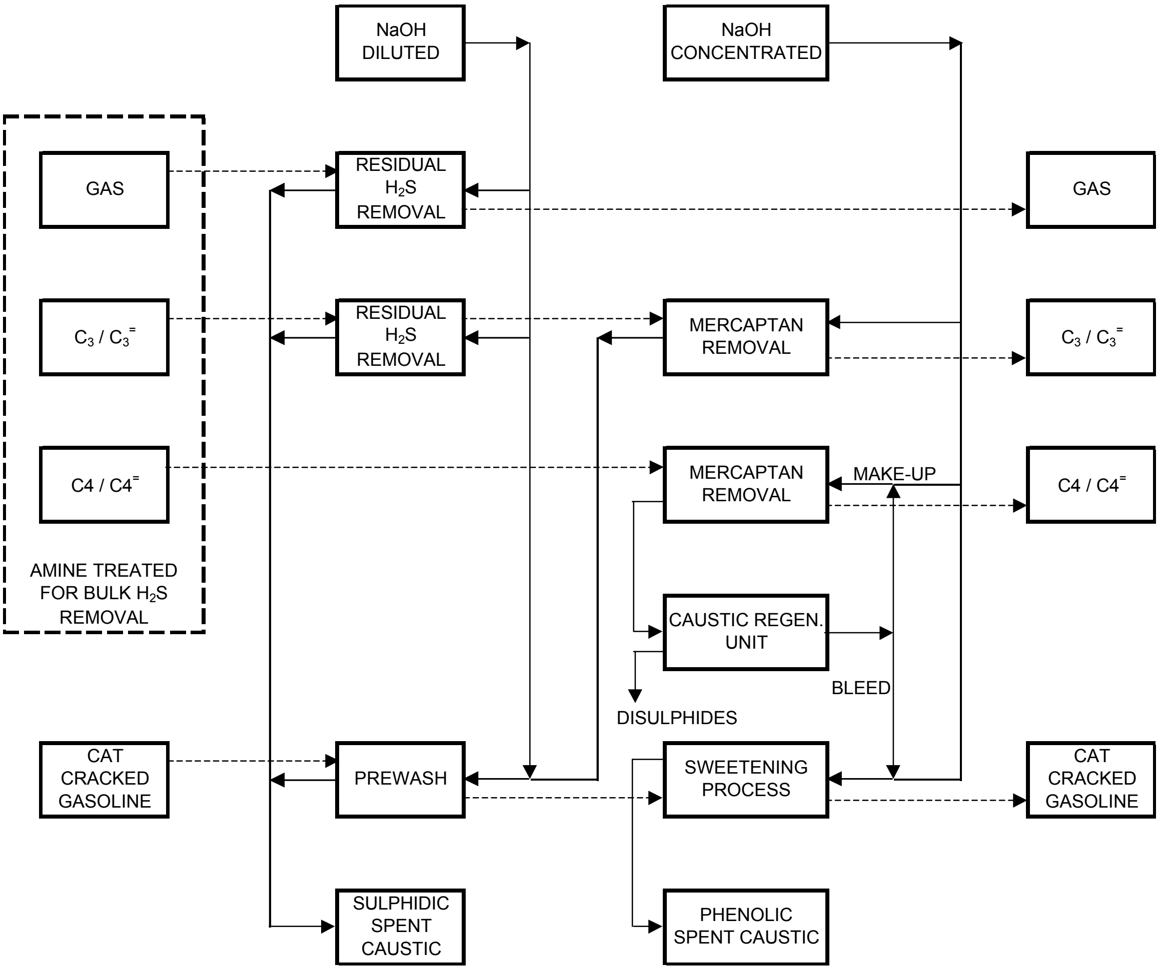
leaded/unleaded scales
rust

Construction/ demolition debris

scrap metal
concrete
asphalt
soil
asbestos
mineral fibres
plastic/wood

Spent chemicals	laboratory caustic acid additives sodium carbonate solvents MEA/DEA (mono/di-ethanol amine) TML/TEL (tetra methyl/ethyl lead)
Pyrophoric wastes	scale from tanks/process units
Mixed wastes	domestic refuse vegetation
Waste oils	lube oils cut oils transformer oils recovered oils engine oils

APPENDIX IV.2 - CAUSTIC CASCADING SYSTEM



APPENDIX IV.3 - TYPE OF INCINERATOR VERSUS TYPE OF WASTE

Typical Oil Content		**Rotary Kiln**	**Multiple Hearth or Single Rotary Hearth**	**Fluidised Bed**
30-100%	**Mainly Oil:**			
	Waste oil, pumpable crude tank sludge	No	X	X
	Acid tar (N.B. consistency varies widely)	X or No	No	X
5-30%	**Medium Oil Content:** (after pre-treatment and homogenisation)			
	Gravity separator and desalter bottom sludges			
	a) if pumpable	X	X	Yes
	b) if too solid to be pumpable	Yes	Yes	No
	Recovered oil tank interface sludge	No	No	X
0-5%	**Low Oil Content:** (after thickening and/or dewatering) Flocculator and/or excess biological sludge	X	Yes (X)	Yes
Solids		Yes	Yes	X
Oily earth		Yes	No	No
Oily stones etc.		X	No	No
Bitumen		Yes	X	No
Oily rags etc. or domestic refuse		Yes	X	No

X= Not really suitable but can accept moderate quantities with care if the type of incinerator has been chosen primarily for a different type of waste.

best available techniques to reduce emissions from refineries - soil and groundwater

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ABSTRACT

This report is one of a series prepared by CONCAWE on the available technologies for environmental protection in the oil refining industry. It describes the available technologies for protecting soil and groundwater from pollution and summarises actual data on facilities installed in refineries, their capital and operating costs, and design performance capabilities. It is intended to be part of the input for the development of BAT Reference Documents (BATREF) required under the Integrated Pollution Prevention & Control (IPPC) Directive.

KEYWORDS

BAT, best available technology, BREF, cost, emissions, groundwater, IPPC, oil, pollution, refinery, sludges, soil contamination, wastes, waste water, water

NOTE
Considerable efforts have been made to assure the accuracy and reliability of the information contained in this publication. However, neither CONCAWE nor any company participating in CONCAWE can accept liability for any loss, damage or injury whatsoever resulting from the use of this information.

This report does not necessarily represent the views of any company participating in CONCAWE.

CONTENTS

V.1. INTRODUCTION

This document is one section of a combined report prepared by CONCAWE on the available technologies for environmental protection in the oil refining industry. It is intended to be part of the input for the development of BAT Reference Documents (BATREF) required under the Integrated Pollution Prevention & Control (IPPC) Directive. [1]

Environmental controls are normally costly, and costs have ultimately to be borne by the consumer in terms of increased prices. It is clearly necessary to establish controls on the basis of sound science, risk assessment and cost/benefit and environmental need considerations. This section of the CONCAWE report specifically considers the range of techniques which could be considered as Best Available Techniques (BAT) for use in European refineries to protect soil and groundwater from pollution; also the cost of installing them.

In **Section I**, it is pointed out that there is no such thing as a universal “BAT”. This is particularly true for the protection of soil and groundwater. Virtually all the techniques employed fall into the categories of either maintenance or retrofit. Both the techniques chosen and their costs depend very heavily on the type of facilities already installed and their condition, and the underlying geology of the site, particularly the groundwater regime. Costs of the various techniques, and the choice of suitable technique can only be made on a case by case basis for each site.

The materials handled during the refining of crude oil into products, if lost to the ground, can result in impaired suitability of soil and/or groundwater for certain uses. Current refinery operating practices are designed to minimise the potential for such loss. There are therefore two aspects of contamination of soil and groundwater that are appropriately addressed in the context of BAT. The first is the prevention of the loss of contaminants to soil and groundwater, and the second addresses the management of soil and/or groundwater that has been impacted by historical product losses.

The sections below related to the minimisation of the loss of contaminants to soil and groundwater will be discussed in technique/technology-specific terms similar to those utilised in the other sections of this report. With respect to the management of soil and groundwater which are already affected, the discussion is restricted to the appropriate way to approach the question of what level of site rehabilitation is needed to make it fit for the use for which it is intended. A technology by technology comparison of the methods available for cleaning soil and or groundwater if and when that is determined to be necessary is not given. This is because rehabilitation is not normally part of the operating permit for a plant on which the BREFs are intended to give guidance; and also, the selection of an appropriate approach is so contaminant and site specific that it would be virtually impossible to make generalisations about the technical suitability of any one technique, the level of performance it would achieve, and the cost incurred.

While the issue of site specific implications is also valid for the other environmental media discussed in this report (i.e. air, waster, and waste) the nature of the actual emission sources is much more similar between refineries than is the nature of the soils, geology and hydro-geology, contaminant type and age, etc.; all of which are additional considerations when dealing with contaminated land. What is important in regards to BAT for contaminated land management is how to determine what quality the soil and groundwater needs to exhibit to be appropriate for the use to which it is being or is intended to be put.

V.2. SOURCES OF CONTAMINATION OF SOIL AND GROUNDWATER

The main sources of contamination of soil and groundwater by oil are typically those places along the handling and processing train of crude to products where hydrocarbons can be lost to the ground. These are most commonly associated with the storage, transfer, and transport of the hydrocarbons themselves or of hydrocarbon containing water. Hydrocarbons can enter the ground in three main ways:

- through leaks from tankage (above ground and underground), piping, and/or oily water sewers
- from accidental spills during normal operations
- through poor operational practices during sampling, tank water drawing, or equipment cleaning, etc.

Methods to prevent such contamination are described below in **Section V.3**.

The possibility of contamination by other substances such as contaminated water, catalysts and wastes also exists. As far as contaminated water is concerned, the preventive measures are basically the same as for oily waters. For catalysts and wastes, prevention mainly relies on correct handling procedures. These are considered in the companion section of this report on waste minimisation (**Section IV)**.

V.3. SOIL AND GROUNDWATER POLLUTION PREVENTION TECHNIQUES

The first principle in preventing the pollution of soil and groundwater is to stop potential contaminants contacting the ground in the first place. This requires attention to avoid both operational discharges to the ground and accidental leaks and spills.

V.3.1. OPERATIONAL DISCHARGES

In the past, some operational procedures involved the discharge of what is today viewed as possibly contaminated water onto the ground and then into the drainage system to be treated in the site effluent treatment facilities. This was in accordance with the scientific knowledge and legal requirements of the time. Such practices are now in many cases avoidable. Typical examples with possible corrective actions (most of which come under the general heading of good housekeeping) include:

Sources of Contaminated Water	**Corrective Actions**
Draining water bottoms from tanks onto the ground	Connect drain points directly to the sewer system
Leaving sampling points running	Provide enclosed sampling loops
Cleaning contaminated equipment in unprotected areas	Clean only in specially constructed and dedicated areas
Stripping (draining of residual contents) of road / rail tankers onto ground	Provide dedicated drainage systems

V.3.2. ACCIDENTAL SPILLAGES

Some accidental spillages can be of a continuous nature such as:

- leaking pump seals
- leaking valve glands
- leaks from pipework etc.

or others which are of a one-off nature can occur from sources such as:

- equipment failures
- overfilling of tanks
- overfilling of road and rail cars

Continuous spillages can be controlled by the use of more equipment with appropriate design / construction standards coupled with an effective maintenance programme. Even so, leaks will still occur from time to time. To minimise the effects of these, an effective inspection and monitoring regime is required to ensure early detection and correction. The risk of overfilling can be minimised by both operational procedures and the provision of overfill protection devices. Equipment failure is best guarded against by an effective inspection system.

V.3.3. REGULAR INSPECTION SYSTEMS

Refineries typically have a system for regular inspection of major items of equipment such as pressure vessels, heaters, tanks etc. The purpose of these is to identify potential sources of failure before they occur so that corrective action may be taken.

Such systems may be supplemented by additional testing for leaks etc. as appropriate. Such test methods include acoustic surveys of tanks, dye testing, flammable gas testing, etc.

V.3.4. GROUNDWATER MONITORING

Part of the procedure for management of soil and groundwater is monitoring for contamination (mainly by oil). Such surveys can be conducted on a one-off basis and there are many methods for conducting them. However, it is also possible to have an on-going monitoring system consisting of periodic sample collection and analysis from one or more monitoring wells. Such wells can also be adapted for oil recovery if contamination is discovered.

Numbers and locations of any monitoring wells are dictated by their purpose and the local geohydrology of the site. Groundwater monitoring is also being considered in certain locations as part of leak detection systems for some types of equipment (e.g. sewers and tanks). These uses are described in the relevant following sections.

V.4. TECHNOLOGIES TO PREVENT POLLUTION OF SOIL AND GROUNDWATER

Preventative techniques available to reduce the likelihood and severity of any hydrocarbon losses into the ground are related to the source from which the loss would potentially occur. The control techniques which may be considered as BAT are described below for the various categories of equipment or operations.

V.4.1. PROCESS AREAS

Areas around process equipment are normally paved with concrete and drained to the site effluent treatment system, both for ease of working and to protect the underlying soil from contamination. Even so, it is important that such areas are kept clean and that any oil spilt is cleaned up as quickly as possible. The concrete must be kept in a good state of repair and the sealing of joints maintained.

There is a balance in deciding the area to be covered in this way. At one extreme, it might be thought that all areas where there is any possibility of contamination should be paved. However, particularly in areas of high rainfall, a large paved area would mean that excessive quantities of normally clean water would pass to the effluent treatment system and overload it so that paradoxically this can lead to the volume of oil discharged to the surface water increasing.

V.4.2. SEWER SYSTEMS

Sewers are an integral part of the operations of a refinery. They serve to transport waters generated during refining operations or collected (e.g. rainwater) safely to the refinery's wastewater treatment facilities or to offsite discharge depending on their quality. Sewers are also an integral part of the refineries safety system as they must be able to carry off waters generated during any emergency firefighting situation that could occur. Sewers can contribute to contamination of soil and groundwater if they leak hydrocarbon-containing waters to the surrounding soil/groundwater. The methods of controlling hydrocarbon leakage from sewers are all related to minimising the potential for this to occur.

As with all of the BAT items presented throughout these reports, there can be significant differences in the cost of control depending on site specific situations and whether the application is a retrofit or grass roots installation.

It is important to keep in perspective the magnitude of sewer systems in a refinery when discussing BAT for sewers. It is not uncommon for a typical refinery to have 50 km of sewers. At a single site these will also consist of varying diameter pipework, construction materials, ages, composition of water being transported, and location relative to the groundwater table. A vital aspect of developing a realistic BAT approach to sewers is to view them as a system in which appropriate attention is given to those segments at highest risk of leaking hydrocarbons to the soil, while not making unproductive use of resources protecting or inspecting sewers not likely to impact their surroundings. An example of this are sewers which are always located below the groundwater table which would not contribute to contamination of their surroundings, since any leakage would be into, rather than out of, the sewer. Inspection frequencies should be established taking into consideration the probability and significance of any leak that might occur.

V.4.2.1. Routine Sewer Inspection / Leak Detection

Inspection of sewers is the most common means of protecting against leakage of contaminated waters to the surrounding soil. There are numerous means of testing the integrity of a sewer, the most common means of which is by video camera. The cost for such an inspection can easily run at 5 to 50 EUR per meter. However, this is only a fraction of the actual cost of sewer inspection since the majority is often associated with the isolating and cleaning of the sewers prior to inspection, and disposal of the sludges removed from them. Experience indicates that when all of these costs are factored in (depending on the regulatory requirements on the disposal of the sludges) camera inspection can run in the range of 100 to 400 EUR per meter. Despite this very high cost the camera can not identify leaks; it can only identify defects such as holes and cracks in the sewer. Depending on the severity of the crack, the nature of the soil immediately outside the pipe (i.e. clay), the location of the defect in the pipe, etc. the defect may in fact not actually be a source of leakage.

Perhaps the most effective means of testing for leakage is a simple hydrostatic head test of the sewer. While this method will not indicate where along a sewer line a leak is located, it will indicate the presence of a leak. Importantly it can be done without the costs associated with the cleaning of the sewer. It is also applicable to sewers of any diameter while there are variable lower diameter limits on any technique which requires inserting instrumentation into the sewer. However, applying increased pressure to a sewer does give rise to a risk of causing leaks.

V.4.2.2. Novel Technologies

Two new sewer inspection techniques are being developed that have significant potential advantages over the current use of cameras for leak detection but these are not yet commercially proven. One of these does actually detect leaks rather than defects. Both of these techniques have the advantage of allowing inspection to be carried out without prior cleaning.

Electrical Current

In this method, a probe is pulled through the sewer pipe which detects leaks by sensing where an electrical current flows with the water through the leak. The sewer must be full of water for testing. As the probe is pulled through the sewer, a signal is recorded when it passes a point of leakage. The technique is applicable to sewers made of plastic, clay, and concrete (including, reinforced) but not metal. The cost saving associated with not having to clean sewers in advance of testing and only detecting leaks rather than defects which may or may not be a leak source, are likely to be significant.

Acoustic

Acoustic technology can be used to inspect all types of sewer pipes. As it is pulled through the pipe, the measurement device generates an acoustic wave signal in the pipe itself and then receives the signal back. Using specially developed software, it can determine the presence of a discontinuity in the pipe integrity which like the camera technology may be indicative of a leak. The advantage over a camera is that sewers do not need to be cleaned in advance of testing. The instrument can be pulled through build-ups of sludge and generate the required signals in its presence.

V.4.2.3. Secondary Containment

Secondary containment by installing below ground sewers in an impermeable conduit (i.e. a double wall pipe, membrane-lined hole, or concrete entombment) is not feasible for existing sewers. Its cost is also likely to outweigh any likely benefit derived over a well maintained/inspected traditional sewer system in all but the highest risk situations.

V.4.2.4. Above Ground Sewer Construction

New sewer construction for process waters can be built above ground which ensures the ability to easily detect leakage visually. Replacing existing sewers with above ground sewers is generally impractical due to infrastructure constraints and the fixed costs already committed to the below ground sewer network. Use of above ground sewers also will increase facility energy requirements due to the likely need to provide pumping capacity for waters which in below ground sewers are gravity flow systems.

V.4.2.5. Segregated Sewer Systems

Keeping clean (i.e. acceptable for discharge/non-hydrocarbon containing) sewers segregated from process water sewers can significantly reduce the length that carries water which if released could contaminate adjacent soil and groundwater. Additionally such segregation is likely to result in significant savings in the size of refinery wastewater treatment facilities. Sewer segregation is not likely to be practically applied in a retrofit situation for obvious reasons.

V.4.2.6. Minimising Sewer Length

To the extent practical it is preferred to minimise the length of sewer lines carrying contaminated water. This reduces the length over which a leak can occur and also the length of sewer potentially subject to costly inspection procedures.

V.4.2.7. Materials of Construction

The material used to construct the sewer and any jointing materials used must be determined to be compatible with the water to be conducted. In particular they must be resistant to any corrosion/erosion likely to exist.

V.4.2.8. Groundwater Monitoring

Monitoring of groundwater downgradient of sewers known to contain hydrocarbons is a means of determining if there is any suspicion of leakage from the sewers. If there is no detectable concentration of contaminants in the soil/groundwater down gradient of a sewer it is unlikely that the sewer is leaking. This method has the merit that it looks for the presence of leakage and not simply defects in the sewer as is done using camera inspection. Even though a camera image may indicate a crack or hole in a sewer there is no certainty that there is any leakage of contents from the sewer. If the defect is above the level at which the sewer flows, or if the sewer is surrounded by a clay soil there may be no leakage despite the existence of a potential leak pathway.

V.4.3. ABOVE-GROUND TANKS

Above-ground storage tanks (ASTs) are used at refineries for holding either the raw feedstock (crude oil) or end products generated by the refinery processes (gasoline, diesel, fuel oils, etc.). Underground storage tanks (USTs) are used much less frequently (if at all) at refineries - primarily for storing fuel for onsite boilers and vehicles, or for capturing liquids at low level drain points. Because of their more widespread application, this section of the report will be devoted exclusively to pollution prevention aspects of ASTs.

The primary subsurface (soil and groundwater) contamination threats posed by ASTs include the disposal of sludges from the bottoms of the tanks, loss of product from the tanks during operations such as tank water drainage, and product leakage to the ground caused by tank or piping failures or overfilling accidents.

V.4.3.1. Corrosion Prevention

ASTs holding either raw feedstocks or end products will be more resistant to corrosion if they are coated with a two component plastic coating on the inside. To avoid corrosion at the underside of the tank bottom, it should be equipped with cathodic corrosion protection.

V.4.3.2. Leak Detection

As with sewers (See **Section V.4.2.8**) one way to protect against soil and groundwater contamination is by detecting leaks at an early stage. Leaks through a tank bottom can be determined through the use of a leak detection system. Conventional systems include inspection ports, inventory control and inspection wells. More advanced systems include electronic sensing probes or energy pulse cables whereby product that comes into contact with the probe or cable will alter its impedance and trip an alarm. In addition, it is common practice to use a variety of inspection procedures on tanks at intervals to prove their integrity.

V.4.3.3. Secondary Containment

This refers to installing additional protection against storage tank releases over and above the inherent protection provided by the tank shell. There are three major types of secondary containment: double tank bottoms; impervious membrane liners and tank farm bund containment. Each of these are described below, and indicative costs are given in **Section V.5**.

Double Tank Bottoms

Installing a second impervious bottom to a tank provides a measure of protection against non-catastrophic releases due to corrosion, faulty weld joints, or flaws in the bottom material or the construction details. In addition to containment, the secondary bottom provides a means of allowing detection of a bottom leak which is not obviously visible to an operator, as a similar shell defect would be.

Double bottoms can either be retrofitted in existing tanks or incorporated into the design of new tanks. If retrofitted, the existing tank bottom is normally used as the secondary flooring, and sand, gravel or concrete can be installed between the new primary and secondary floors. In this case, it is general practice to keep the interstitial space to a minimum and therefore the secondary bottom should slope the same way as the primary bottom. The slopes to the base of tanks can be either flat, cone-up (sloping from the centre down to the tank perimeter) or cone-down (sloping downward from the tank perimeter).

Nearly all tank floors are made of carbon steel. If a double bottom is to be installed (either retrofit or new build), there are choices in material selection for the new floor. A second carbon steel floor can be utilised or a more corrosion-resistant stainless steel floor can be installed. A third choice is to use a glass fibre-reinforced epoxy coating over the steel.

The use of double bottom tanks allows a vacuum system to be installed, and in this case the space between the lower and upper floor is not filled, but retained as an air space using steel spacers (which can typically be a steel reinforcement mesh). In this more recent system, the space between the floors is kept under a vacuum that is continuously monitored. Any leak in the primary or secondary floor will dissipate the vacuum and trigger an alarm. A further test of the extracted air will indicate an upper floor failure if product or vapours are present, or a lower floor failure if neither product or vapour is present (subject to any previous underfloor contamination).

Impervious Membrane Liners

The impervious membrane liner is a continuous leak barrier under the entire bottom surface of the AST. It can be an alternative to a double bottom or it can be added as an extra measure of safety below the double bottom. Like the double bottom, it is primarily intended to arrest the small but persistent leak rather than address a catastrophic failure of the entire tank.

The key to an effective liner is that the seams must be liquid-tight against either the steel shell of the tank or the concrete wall that supports and surrounds the tank. The minimum thickness of the flexible membrane is 1 mm, although 1.5 to 2 mm thick sheets are commonly used. The membrane must be chemically resistant to the product stored in the tank.

Impervious membrane liners are used in lieu of double bottoms in a number of non-European countries. They can be installed either in a new build design or in a retrofit fashion and they generally include a leak detection system. The cost of retrofitting a liner is slightly higher than installing a double bottom as it involves jacking-up the existing tank to install the membrane and leak detection system. As new build construction, an impervious liner may be cheaper than a double bottom, but it may have a higher life cycle cost. This is because any future failures of the liner would require re-lifting the tank or reverting to a new double bottom solution.

V.4.3.4. Tank Farm Bund Containment

Whereas double bottoms or impervious liners protect against the small but incessant leak, an impermeable tank farm bund is designed to contain large spills (for safety as well as environmental reasons), such as caused by a shell rupture or a large spill from overfilling. The bund consists of a wall or dike around the outside of the tank to contain all or part of the tank contents in the event of a spill, and (in some cases) an impermeable ground barrier between the tank and the dike to prevent infiltration of the product into the ground.

The dike is typically constructed of well compacted earth or reinforced concrete. The height is normally sized to accommodate the maximum contents of the largest tank within the volume enclosed by the dike. However this philosophy of total capture is flawed if the ground between the tank and dike is permeable. Oil can permeate downward and under the dike in these situations.

There are a number of ways to seal the ground to prevent downward migration of spilled product. The cheapest is to utilise a low permeability clay that may be naturally present or be imported for the purpose. However, both natural clay and its synthetic counterpart, bentonite, are susceptible to shrinking and cracking under dry conditions, and so measures must be taken to ensure that the material stays moist. In a dry climate it may therefore be preferable to install an asphalt or concrete surface, although care must be taken to ensure that cracks do not develop over time. Another option is the use of a high density polyethylene (HDPE) liner, although the concern here is to ensure the seams are properly bonded during installation. Also, if an HDPE liner is employed, it should be covered with 15 to 30 cm of well graded sand, gravel or soil to protect against damage by vehicular traffic.

A study in the United States [2] has concluded that the effectiveness of liners in protecting the environment is limited because of their unreliability and the difficulty in inspecting or testing their integrity. Also, there are few releases that would be contained by such liners, and moreover, they are expensive to install. Because of this, it was concluded that other preventative measures are more effective in protecting the environment and are more cost effective in the long run.

A final note on impervious barriers within tank bunds concerns rainwater runoff. As the ground is now sealed, a drainage system must be installed to handle the impounded rainwater which would otherwise have percolated into the soil. Best practice at refineries is to segregate this normally clean tank farm storm-water from potentially contaminated storm-water (such as might be generated at pipeline manifold, process or loading areas) in order to minimise the amount of wastewater processed through the facility’s oily water treatment system. Only if the water is oil contaminated should it be passed to the effluent treatment system. However retrofitting segregated systems is not usually feasible.

V.5. OVERALL SITE MEASURES

As well as protecting the soil and groundwater under individual parts of the site, measures have been taken in some cases to prevent groundwater contaminated with free oil leaving the site and polluting either ground or surface water outside. This has the effect of containing any contamination and allowing it to be cleaned up either as part of an ongoing programme of site remediation or when the site is finally closed and turned over to some other purpose. In the latter situation more invasive methods of treatment can be used. In one or two cases, such measures were implemented when the refineries were constructed. In other cases, they have been implemented at a later date.

There are two main types of such measures, physical barriers or hydraulic control. The choice of which method to use and its details is governed by local factors such as location, topography, relationship to surrounding areas, and particularly local geology and hydro-geology. The two types of measure can also be combined.

V.5.1. PHYSICAL BARRIERS

Physical barriers such as clay walls or plastic membranes can be installed around the site boundary. To be effective at containing oil pollution, these have to extend below the water table. Monitoring wells will also be required to ensure that if oil does build up behind the barrier, it can be removed before it has a chance to escape under the barrier.

A second form of barrier is a ditch also extending to below the groundwater table. Any oil leaving the site can be observed floating on the water in the ditch and recovered. The outer face of the ditch can be sealed with an impervious layer such as concrete, plastic, clay, steel piling etc.

While both of these measures will prevent free oil floating on the groundwater surface leaving the site, they do not protect against dissolved contaminants.

V.5.2. HYDRAULIC BARRIERS

Groundwater, like surface water basically flows downhill. Therefore, groundwater can be prevented from leaving a site by lowering the level inside the site by pumping so that it is lower than the level outside. Water will then flow into the site rather than outwards.

The pumped water has obviously to be disposed of. It may be possible to use this water for supply purposes on site. If it is to be discharged, then monitoring will be required to ensure that it is not contaminated. If it is, then it will have to be treated in which case, this method will be limited by the capacity of the effluent treatment system.

V.6. MANAGEMENT OF CONTAMINATED LAND

There are a significant variety of techniques and technologies available to remediate contaminated land and groundwater. They are in many cases very site specific, and affected by the nature of the contaminant, the physical site characteristics, and the regulatory context in which they occur. This report therefore identifies the approach that should serve as BAT for an assessment of what level of remediation a site requires. Those in charge of individual projects should be left to assess which approach leads to the required standard of soil and groundwater quality in the most cost effective manner.

Descriptions of many of the available contaminated land and ground water management technologies are available in the open literature on this subject. They cover a wide range of techniques including: in-situ or ex-situ; chemical, physical, and biological; very disruptive of the environment to very non-intrusive, etc. The choice will be more governed by site specific considerations than is typically the case with the techniques described for other media in this report. The most difficult part of Contaminated Land Management is typically the determination of what constitutes a condition fit for the use to which the land / groundwater is to be put, rather than what technology is most appropriate to achieve this goal.

The methodology that qualifies as BAT for assessing what constitutes the conditions of a site that make it fit for its intended future use is the use of Risk Assessment and Risk Management: i.e. Risk Based Contaminated Land Management. A Joint Statement to this effect has been issued by the EC Concerted Actions groups, NICOLE and CLARINET, in October 1998. In this document, these networks (industry and authority driven respectively)

> *"present the common view that risk based approaches are vital to allow governments and industry to deal with contaminated land. The current state of the art provides an effective set of tools for better decision making now. It is therefore important to disseminate the state of the art and encourage widespread use of Risk Assessment and Risk Management tools. Moreover cleaning up all sites to background levels suitable for the most sensitive possible land use (the concept of 'multi functionality') is not technically or financially feasible."*

Soil and groundwater need to be evaluated in terms of fitness for use for their intended present and future uses. Risk assessment and risk management, typically consisting of a tiered system of less conservative assumptions and more intensive data availability (yielding equally protective results for human health and the environment) are the technology that make this possible. This approach to contaminated soil and groundwater management should be identified as BAT and is described in a CONCAWE report. [3]

V.7. COSTS

Although some cost data for installing measures to protect against soil and groundwater contamination was supplied by refineries, this data was limited and it is not possible to establish firm costs. Costs in this area are extremely variable, even more so than for the installation of other types of emissions control. The figures quoted below should therefore only be considered indicative.

V.7.1. SEWERS

One refinery reported that the cost of replacing or lining approximately 320m of sewer cost 1600 EUR/m whereas another installed 710m of above ground epoxy resin sewer at a cost of 1500 EUR/m. In a third case, the renovation of 300m overground sewers cost 300 EUR/metre.

V.7.2. TANKS

V.7.2.1. Double Bottoms

Typical retrofit costs for double bottoms, as quoted from German or Swiss suppliers, are as follows and include provision of a vacuum leak detection system:

- Carbon steel: 110 EUR/m^2
- Stainless steel: 190 EUR/m^2
- Glass fibre-reinforced epoxy: 175 EUR/m^2

A UK refinery reported that the actual cost of installing a double bottom on a 10340 m^3 tank was 600 000 EUR.

V.7.2.2. Impervious Membrane Liners for Tanks and Bunds

The cost of retrofitting a liner is slightly higher than installing a double bottom as it involves jacking-up the existing tank to install the membrane and leak detection system. An indicative cost is of the order of 200 EUR/m^2. As new build construction, an impervious liner may be cheaper than a double bottom, but it may have a higher life cycle cost. This is because any future failures of the liner would require re-lifting the tank or reverting to a new double bottom solution.

The following are per unit costs for placing the following materials on the ground, :

- Clay: 13 EUR/m^2
- Asphalt: 24 EUR/m^2
- Concrete: 30 EUR/m^2
- Bentonite: 18 EUR/m^2
- HD Polyethylene 23 EUR/m^2

This excludes the cost of lifting the tank for installation. However, costs of placing such materials in the floors of bunds would be of this order. An additional cost arises from moving any pipework in the bunds.

For comparison of the installed costs of such a liner, one refinery reported that since 1994, it had installed a clay bottom liner under each lifted tank during maintenance. A leak detection system was installed at the same time. The cost of this was about 20 000 to 30 000 EUR per tank with the cost of the clay liner being 11 to 17 EUR/m^2. The total cost for 14 tanks has amounted to 350 000 EUR. A similar cost (35 000 EUR) was quoted in another installation of an impervious liner (plus leak detection) for a 12 000 m^3 concrete tank.

Other refineries have quoted the total cost for installing concrete paving under 6 big tanks at 1 300 000 EUR (220 000 EUR per tank), the cost of sealing bund dike walls with asphalt (around 10 tanks) at 800 000 EUR, and the cost of concrete paving bunds at 70-140 EUR/m^2.

V.7.2.3. Tank Leak Detection and Inspection

One refinery reported that the installation of a leak detection system on a group of four 12m diameter tanks cost a total of 55 000 EUR with an operating cost of 4000 EUR per year.

The routine inspection of tanks at another refinery was quoted as 2 000 EUR per year.

V.7.3. SITE BOUNDARY BARRIER

One refinery quoted the cost of installing 200m of impermeable HDPE barrier along the site boundary at 150 000 EUR (750 EUR/m).

V.7.4. MONITORING

Quoted costs for installation and operation of monitoring wells was highly variable ranging from 25 000 EUR for 100 wells (250 EUR per well) to 140 000 EUR for 50 boreholes (2800 EUR per well) but with a minimal operating cost.

Costs of groundwater monitoring systems were quoted as 1400 EUR per year for 18 wells (78 EUR per well) in one case to an average of 45 000 EUR (including 7000 EUR for analysis) for three surveys at intervals of some years.

V.7.5. TOTAL COSTS

In a number of cases, refineries quoted their total costs for a number of years for a variety of measures to protect soil and groundwater. These ranged from 1 900 000 EUR over eight years at one refinery to predicted investments of 2 500 000 EUR per year at another.

V.8. REFERENCES

1. EU (1996) Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. Official Journal of the European Communities No. L257, 10.10.1996

2. API (1998) A survey of diked-area liner use at aboveground storage tank facilities. API Publication No. 341. Washington DC: American Petroleum Institute

3. CONCAWE (1997) European oil industry guideline for risk-based assessment of contaminated sites. Report No. 2/97. Brussels: CONCAWE