9.2

Environmental management in refineries

9.2.1 Introduction

Environmental economics, which analyses the links between economic activity and environmental systems, has hypothesized that a relation which may be described as an 'inverted U' exists between environmental quality/pollution and *pro capite* income variables (Kuznets hypothesis; Kuznets, 1955). According to this hypothesis, when income begins to grow, starting from a low level, the environmental impact first increases to a maximum corresponding to a certain income value, and then starts decreasing. In substance, the dichotomy between economic growth and environmental protection is said to exist only at low income levels and instead, at higher levels, to become a synergy. It would seem, therefore, that by increasing income levels, a future of sustainability may be envisaged. This hypothesis is, moreover, a plausible one; as with economic growth, environmental externalities become more and more evident and induce the competent authorities safeguarding public environmental assets to intervene with increasingly restrictive regulations and provisions. Even though the supplementary investments to be made and the additional operating costs penalize, to a certain extent, the sector that sustains them, at the same time a fresh demand for goods and services is generated which contributes towards overall economic growth. The historical evolution of the refineries – and more generally of the energy sector – is a good demonstration of this theory. Indeed, refineries are set up in the first phase of a country's development, helping it to grow both economically and socially, and continuing this support throughout its post-industrial development phases. Many refineries currently operating are more than 50 years old, and are expected to operate for a long time to come. Although accurate environmental auditing has only been introduced in the last few decades, historical experience allows it to be stated that the environmental impact of refineries, for the same output, has systematically diminished, thanks to management based on continuous improvement.

The environmental impacts of a refinery are both direct and indirect; in this chapter only the former are considered. Indirect impacts are in fact connected with the final use of petroleum products and pertain not so much to the environmental management of a refinery, as to its overall configuration and to the integration of the various processes that determine the ecological quality of the products. Direct impacts, on the other hand, are generated by processing units and by the activities carried out within the refinery.

Refineries are highly complex industrial plants containing numerous integrated process units, with a vast range of possible configurations. They differ in size, complexity of the processes used, flexibility of the loads that can be treated, and typology and quality of end-products. Furthermore, they are diversified in terms of production strategy (linked to market demand), age and historical evolution, and lastly the availability of infrastructure and services for the local environment.

Considering the complexity of the processes applied to the oil in order to attain the formulation and distribution of the derived products, it is not surprising that a refinery covers a large part of the spectrum of possible environmental impacts. The map of impacts relating to a refinery is shown in **Table 1**, broken down into the basic environmental matrixes: air, water and soil. These impacts occur at various scales: local, with effects on the work place and on the surrounding territory and community; regional, for example in the case of acid rain, photochemical smog and waste disposal; and global, with special reference to the emission of greenhouse gases. To mitigate these

Table 1. The main environmental impacts of a refinery

Environmental matrix	Pollutant
Air	SO_2, NO_x, CO, CO_2, VOC, H_2S, BTEX, NH_3, CS_2, HF, metals (Ni, V and others), powders from energy production plants (60% emissions), furnaces, catalytic cracking
Water	Hydrocarbons, NH_3, phenols, H_2S (CONCAWE, 2004)
Soil	Hydrocarbons, dangerous wastes, spent catalysts, coal dust, reservoir/tank dregs, process treatment sludges (IPPC, 2003)

Table 2. The main environmental regulations concerning refining

Environmental matrix	European directives
Air	IPPC 96/61/CE, 2001/80/CE, 2002/3/CE, 2003/87/CE
Water	IPPC 96/61/CE, 200/60/CE
Soil and wastes	IPPC 96/61/CE

impacts, increasingly strict regulations have been developed, more and more aimed at global scale.

Table 2 shows the main European environmental regulations, with which those of the United States are substantially in line. Of particular importance is the European Directive Integrated Pollution Prevention and Control (EIPPCB, 2003), which introduces integrated environmental authorization for the main industrial installations, including refineries.

Environmental protection is a central theme for refineries because, as large industrial sites, they are generally the prime source of pollution in the areas where they are located. Moreover, when refineries were first set up, they occupied areas which were not densely populated, but subsequent urbanization has progressively modified the hinterland further aggravating both environmental problems and those connected to the territory and relations with the local community. In general laws and regulations govern the responses to environmental problems. However, pressures exerted by the community – lobbies, environmental organizations, public opinion, shareholders and financiers – and the introduction of new technological and operating standards and of market instruments (taxes enabling environmental externalities to be internalized) increasingly point towards the evolution of environmental standards. In this case the environmental variable becomes a strategic component, a competitive advantage and an important factor in terms of development and technological innovation. On the basis of this proactive behaviour, the most important objectives for refineries in terms of environmental management are: *a*) implementation of environmental accounting and management systems aimed at continuous improvement; *b*) increased energy efficiency and the concomitant reduction in emission of greenhouse gases; *c*) reduction of emissions into the atmosphere (nitrogen and sulphur oxides; heavy metals and particulate; and volatile organic compounds); *d*) recovery of contaminated soils and prevention of water and soil contamination.

The objectives of environmental improvement can be achieved by adopting the Best Available Technologies (BAT) in existing plants. In choosing these BAT it must be borne in mind that some of them can be used only in new plants, as not all of them are suitable for modernizing existing plants. Replacing a technology already in use with one that is more respectful of the environment can in fact entail unsustainable economic costs (for example, the decommissioning of the existing plant and a lengthy interruption in production). It is also true that, in view of the considerable differences between refineries, the set of measures to minimize emissions at acceptable costs can vary, sometimes greatly, from one refinery to another. Generally speaking, the main aspects of environmental management in refineries concern: *a*) the integrated environmental management system; *b*) the management of emissions into the atmosphere; *c*) the management of water discharges and safeguarding of waters; *d*) waste management and the prevention of soil contamination; *e*) the environmental monitoring system.

9.2.2 Environmental management system

The Environmental Management System (EMS) is the basic instrument for managing the environmental aspects connected with an installation and for aiming at the continuous improvement of the performance indexes. EMS foresees the definition and implementation of a formal environmental policy regarding the environmental implications of all activities, so as to guarantee: *a*) the identification of significant environmental aspects and impacts, and of quantitative improvement objectives; *b*) the definition of relevant action programs and indicators for ascertaining their effectiveness; *c*) program implementation and operative control; *d*) monitoring of results and any corrective actions; *e*) training and improving personnel awareness; *f*) auditing and re-examining the overall program, with the definition of new objectives and start-up of the new improvement cycle; *g*) external communication.

The environmental management system uses two main instruments: the EMS manual and the environmental procedures annexed to it which specify how, by whom, when and with what means the actions described are put into practice. The EMS manual generally includes: *a*) the environmental policy and improvement plan, with relevant programs and objectives; *b*) a description of the organization of the refinery, of the means, activities and responsibilities regarding environmental preventive measures, protection and improvement; *c*) identification of the environmental implications deriving from the industrial activities of the site under normal, anomalous and emergency conditions, and an evaluation of their significance; *d*) identification of the legislative provisions and of the best environmental practices applicable to the activities of the refinery; *e*) planning and documentation of operative control and of environmental monitoring and surveillance activities; *f*) registration of non-conformities and planning of any corrective and/or preventive actions.

In formulating the environmental management system, the initial analysis of the environment must take into consideration all the activities carried out on the site, with particular reference to: reception (supply and internal handling), storage and distribution of incoming raw materials and outgoing products; the operation of the process plants and of the main auxiliary refinery plants, such as for example the cogeneration plant and the effluent treatment plant; to other refinery activities, such as laboratories and technical services (maintenance, inspection and/or tests and management of other companies). For each of the activities recognized to be of environmental interest it is necessary to identify and analyse the correlated aspects, i.e. the specific interactions of each activity with the environment. This analysis therefore concerns both the direct environmental aspects, i.e. those linked to refinery activities under direct managerial control, and indirect ones, over which the refinery may not have total management control. In particular, a refinery, in order to also guarantee correct management and control of indirect impacts, must define specific modalities of intervention by contractors, through:

- The definition of operating practices and models of behaviour that must be respected by all personnel of companies operating in the refinery, during activities that could give rise to impacts on the environment (e.g. loading and discharging of ships, waste management, losses or spilling of chemical substances or petroleum products), by means of environmental procedures and specific instructions, to be distributed to third parties before they start operating in the refinery.
- Periodic training and information meetings with the participation of the companies (site managers) on subjects pertaining to safety and environmental protection.
- Continuous control and checking of the conformity of the activities performed by the companies present in the refinery (transportation of products by sea and overland, site areas, maintenance measures) and whatever is foreseen by the environmental management system and in the relevant documentation.

Once the direct and indirect environmental aspects have been identified, an assessment is made of the extent of possible impacts, bearing in mind: *a*) environmental values and policy; *b*) the main interlocutors advocates of environmental interests of the refinery; *c*) the characteristics of the ecosystems affected by the activities of the refinery; *d*) the trend in time of the data on performance regarding environmental issues.

Environmental management systems are now common in big industrial installations. Advanced international standards have been defined by the ISO (International Standard Organization) and, at European level, by EMAS (Environmental Management and Audit Scheme). The proper implementation of these standards is periodically certified, to ensure constant attention to management and a continuous trend towards improvement.

9.2.3 Management of emissions into the atmosphere

One of the most important impacts on the environment produced by refineries is emissions into the atmosphere, made during the refining processes. Emissions into the atmosphere take the form of: stack emissions, fugitive gas emissions, accidental losses, and losses due to plant maintenance.

Energy production plants, furnaces and catalytic cracking are the sections of the refinery responsible for the largest stack emissions of carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), particulate, and sulphur oxides (SO_x). Typically, 60%

of emissions into the atmosphere originate from energy production processes. Sulphur recovery units, flares and the regeneration of catalysts represent minor sources of emission of the same pollutants. The main sources of losses and/or fugitive emissions of Volatile Organic Compounds (VOCs) are storage units, product loading and handling, oil/water separation operations (discharge water treatment plants), as well as losses of flanges, valves, seals and drainage. Other substances emitted into the atmosphere to a lesser extent are hydrogen sulphide (H_2S), ammonia (NH_3), toxic and dangerous pollutants such as BTEX (Benzene, Toluene, Ethylbenzene, Xylene), carbon sulphide (CS_2), hydrogen fluoride (HF) and the metals (e.g. Ni, V) contained in the particulate.

For the management of emissions into the atmosphere, a regulating instrument is adopted in various countries of the European Union; the so-called ‘bubble’ approach, generally applied to emissions of SO_x into the atmosphere and often extended also to emissions of NO_x, powders (metals contained in them) and CO. The bubble approach regards the refinery as a single unit. Therefore the control of conformity with the emission limits fixed by legislation is not based on the emissions of a single plant, but on those of the refinery as a whole, allowing for the composition and flows associated with all the sources of emissions included in the ‘bubble’. The application of this approach is based on technical, economic and environmental considerations. Its technical justification derives from the complexity of the plants and from the integration of the various processes: the large number of emission points, the technical and economic inter-relations between types of load, types of processing operations, and the variations under different working conditions in relation to the typologies, quantities and characteristics of the various products. From the economic standpoint, the bubble approach enables the refineries to use the fuels produced in their internal processing cycles in a flexible manner, in the various plants and at different moments. This makes it possible to: identify the most efficient and economic solution for reducing emissions; to adapt to the market, to the availability of crudes and to the variability in demand/supply of petroleum products; and to operate effectively in a competitive context.

For a correct and effective application of the bubble approach, the emission levels have to be defined in a transparent and clearly quantifiable manner. In general, stack emissions derive from the combustion of oil and/or combustible gases in the furnaces of the refinery process plants. The use of the two different fuels involves a diversification in quality and quantity of the pollutants emitted in the fumes, in particular in relation to the sulphur content.

Global management of SO_x emissions

Sulphur is a component which is intrinsically present in the crudes processed in the refinery. All the sulphur entering the refinery with the crude can leave it, respecting the material balance, in the form of: sulphur contained in the finished products; sulphur recovered inside the refinery in the special recovery plant (Claus plant) or in any other abatement plants; SO_x in the atmospheric emissions generated by the combustion plants (process furnaces, boilers for steam production, gas/liquid turbines, etc.), by certain process units (FCCU, Fluidized Catalytic Cracker Unit; coking, etc.), by the incineration of residual gases containing H_2S not totally recovered in the sulphur recovery plants (Claus, Tail Gas Clean Up) or by the incineration of other residual gases containing H_2S.

The problem of reducing sulphur is thus always studied and addressed in an integrated manner, taking into account simultaneously all possible impacts, limitations and implications with reference to crude supplies, to the product specifications and market, to the environmental benefits obtainable, to the internal recovery capacity of sulphur and to the investments/costs connected with these operations. The total quantity of sulphur entering the refinery depends on the sulphur content and volume in the crude acquired (type of crude). The bubble approach makes the optimum management of sulphur easier as it permits reductions and control of emissions, selecting among the various options those that are operatively and technically most effective, and have the most sustainable incremental costs in each single refinery and in every operational configuration.

Emissions of SO_x due to combustion

The formation of SO_x is determined exclusively by the sulphur content of the fuel, gas or liquid, burnt in the process furnaces and in the boilers for the production of steam. Hence the alternatives for reducing SO_x are the removal of the sulphur from the fuels before their combustion (use of fuels with a low sulphur content), and treatment for the desulphurization of the fuels generated by the combustion process. In this context it is important to consider that the primary technical option is represented by the use of fuels with a low sulphur content. In theory, burning off 100% of the desulphurized gases (without the use of liquid fuels) should reduce to zero the emissions of SO_x due to combustion. In reality, however, the refineries already use all the gas available, generated internally in the various processes, after reducing the H_2S content to a minimum by means of scrubbing in amine treatment plants. These treatment units have variable degrees of efficiency: on average they reach sulphur concentrations (with a 3% oxygen content) in scrubbed gas of around 300-700 mg/Nm^3 and, in some cases, 150 mg/Nm^3 or lower if the gas is used in gas turbines (new treatment plants can reach 150 mg/Nm^3 of H_2S in line with their design specification, but in practice lower values are reached; existing plants, however, can be modified to reduce concentrations to as little as 150-300 mg/Nm^3). This level of sulphur in combustible gas is in any case significantly lower than that contained in a distillate, as for example gas-oil, and 20 to 30 times better than a conventional fuel oil with a low sulphur content (1%).

Improving the efficiency of treatments with amines or other solvents to obtain sulphur contents even lower than 100 ppmv can be another feasible way of reducing SO_x emissions. It must however be remembered that the H_2S removed by the treatment must be conveyed, for recovery, to the Claus plant (see Chapter 3.2) whose total capacity is often already used.

At present no refinery has enough combustible gas available to satisfy 100% of its own requirements for the production of electricity and heat: therefore for the remaining part of its needs liquid fuels are used, such as fuel oil, containing sulphur. A possible alternative is natural gas, but it is necessary to consider local availability, costs, the need to find convenient solutions and purchasers for the fuel oil (it is feasible only in refineries that have a sufficient conversion plant capacity to use the surpluses).

Emissions of SO_x from flue gas desulphurization plants

Flue Gas Desulphurization (FGD) is a so-called secondary technique by means of which SO_x are removed from combustion fumes or from other discharge gases. The SO_x in refinery discharge gases could present concentration levels of 1,500-7,500 mg/Nm^3, prior to treatment. The FGD process often requires the presence of an alkaline absorbent which captures the SO_x and transforms them into solid waste or sludge.

Various FGD technologies are available, with an ample SO_x removal efficiency spectrum. The admission of additives and dry absorption consist in scrubbing processes that remove SO_2 using the same principle as wet absorption (reaction with a calcium-based absorbent): a dehydrated absorbent, generally limestone or hydrated lime, is placed in the combustion chamber; the sub-product is a mixture of sulphites, sulphates and volatile ashes for which no useful applications exist. The admission of additives provides a moderate removal of SO_2 from loads with a low sulphur content. The scrubbing process using seawater uses natural salts contained in the seawater to remove the SO_x. The discharge contains sulphate and chlorine ions, natural constituents of seawater. In other processes, the SO_x are absorbed by adding a jet of ammonia to an aqueous solution, producing ammonium sulphite; this sulphite is subsequently oxidized to form sulphate. The ammonium chloride solution from the scrubbing section is concentrated in an evaporation unit and then granulated. The end product is a potentially marketable fertilizer. The current scrubbing processes with wetted limestone have been greatly improved and are now less complex than the first generation type. Generally, a semi-liquid mixture on a limestone/water base is used as an absorbent; the reaction with SO_x leads to the production of hydrated gypsum. We should lastly recall the SNOX process, based on catalytic reactions and carried out in a refinery in which a mixture of fuel and coke with a high sulphur content is burned; this process has the highest removal efficiency, and has the advantage of combining the removal of SO_2, NO_x and particulate.

Emissions of SO_x from conversion plants

In refineries where there are conversion plants, for example the FCC plant or the coking plant, it can be necessary to reduce emissions into the atmosphere, above all when the environmental conditions or the quality of the surrounding air so require. In such cases the various possibilities are using DeSO catalysts, desulphurizing the load by means of hydrotreating or flue gas desulphurization.

Emissions of SO_x from sulphur recovery systems

The sulphur recovery process is applied to gases with a high H_2S content which issue from scrubbing plants (amine units) and, in many refineries, from the sour water stripper. The H_2S is converted into elementary sulphur in the Claus plant, with yields that reach 99.9%; the residue present in the waste gases after conversion is generally conveyed to the post-combustion unit, with the emission of SO_x.

Management of NO_x emissions

NO_x form mainly through the reaction of nitrogen with the oxygen present in combustion air and, secondarily, through the oxidation of the nitrogen compounds present in fuels.

The techniques to reduce NO_x emissions fall into two categories: primary techniques consisting in the optimization of combustion so as to reduce the formation of NO_x, and secondary techniques, consisting in flue gas treatment to abate the NO_x produced. Generally in refineries the reduction of NO_x emissions is pursued with primary techniques, whereby the control and modifications of the combustion process regard mainly the flame temperature and the oxygen concentration. The formation of NO_x is in fact strongly influenced by the construction characteristics of the combustion plant (boilers or process furnaces), by the type of burners installed, and by the type of fuel used (gas, liquid or solid). With *low* NO_x burners reductions of 40-60% can be obtained for gaseous fuels, and of 30-50% for liquid fuels; with *ultra low* NO_x burners, the reduction can reach 60-70%.

In the combustion process, moreover, there is a direct connection between the NO_x and the emissions of particulate: the reduction of NO_x, as stated, requires a lowering of the flame temperature, which brings about an increased amount of particulate. For *low* NO_x burners using fuel oil, as for conventional burners, a further reduction in the temperature produces not only particulate but also emissions of CO.

Management of emissions of particulate and of CO

Emissions of particulate and of CO in flue gases (from boilers and furnaces) in a refinery are generally very low, unless very heavy liquid fuels with a high ash content are burned. In this last case, considering the availability of internal products, the technical solution generally adopted is to opt for lighter fuels with a low ash content; filters or electrostatic precipitators are very rarely installed. Particulate and CO are generally controlled by optimizing the air/fuel ratio with the use of oxygen analysers installed on the smokestacks: this makes it possible to maximize energy efficiency and minimize emissions. The foreseeable emissions of CO, CO_2 and particulate are variable from case to case, depending on the construction and operating characteristics of the combustion plants and of the corresponding burners. The emissions of metals are linked to the type of crude and the refining processes used. It is possible to reduce metals by monitoring those contained in the liquid fuels and by choosing liquid fuels with a low metal content, whenever this is technically and economically possible.

Management of fugitive emissions

Fugitive emissions, constituted basically by VOC, are produced by the evaporation of light hydrocarbons and derive mainly from: *a*) floating-roof storage tanks; *b*) the seal of pumps for moving light products; *c*) open effluent treatment tanks; *d*) loading operations.

Some examples of instruments useful for the proper management of the problem of fugitive emissions are: methods of estimating emissions, specific instruments for monitoring emissions, modification or replacement of plant components giving rise to losses, implementation of an adequate program to detect and repair leaks, application of techniques for the recovery of vapours during loading/discharge of light products, evaluation of the feasibility of destroying vapours by means of thermal or catalytic oxidation, balancing of vapours during loading operations of volatile products, loading hydrocarbons from the bottom of tanks and tank trucks.

Indicators of emissions into the atmosphere

To monitor the significant environmental aspects of emissions into the atmosphere, the following performance indicators can be used:

- Energy intensity index: this expresses the relation between the ‘energy response’ of the refinery and the ‘standard energy’ response. It is based on benchmarking analyses, i.e. a comparison at international level of performances in the refining sector, and is correlated with the refinery’s performances in terms of quality of end-products, efficiency of combustion in the furnaces in refining plants, and use of fuels.
- COGE (COGEneration) recovery index: this is based on the use of the cogeneration system, consisting of a gas turbine running on residual refining gas and a steam recovery generator; especially designed for the combined production of electrical energy and steam, it permits a reduction in fuel consumption compared with traditional steam production.
- Index of conformity of emissions: this expresses the quality as a percentage of the total emissions conveyed by the refinery smokestacks compared to current legal limits.
- Index of emission per fuel: this expresses the quantity of pollutants emitted per toe of fuel consumed (considering the overall aggregate consumption of fuel oil and gas in the refinery).
- Index of conformity of COGE emissions: this expresses the quality as a percentage of COGE emissions with respect to legal limits.
- Index of air quality of the industrial zone: this expresses in percentage terms the maximum concentration of pollutants in the industrial zone around the refinery, with respect to the limits set by current legislation.

9.2.4 Management of water discharges

Without treatments, the refineries could be among the worst contaminators of surface and ground waters, as their discharge waters may be highly polluted due to the large number of contamination sources with which they come into contact during refining processes. In particular, process waters, steam and washing/scrubbing waters come into contact with the process fluids and therefore contain, in addition to hydrocarbons, both H_2S and NH_3. In a similar manner, cooling waters, although they theoretically do not come into contact with process fluids, may contain pollutants in concentrations which, although low, are in any case such as to cause an environmental problem. Even the meteoric waters which flush the productive areas contain hydrocarbons and should therefore be treated before being discharged.

The pollutants contained in discharge waters derive mainly from: distillation units; visbreaking; treatments with hydrogen; catalytic cracking; hydrocracking; and service units. Discharge waters from refinery blowdown operations may also be contaminated by dissolved gases, some of which are toxic, and may generate foul smells, by suspended solids and by hydrocarbons. The refinery is therefore equipped with a suitable Effluent Treatment (ET) plant. Generally speaking, the ET unit in a refinery receives waters mainly from:

- Drainage of industrial water (from the demineralization system for waters from the boilers, from machinery cooling circuit purges and from industrial waters), the flow of which is conveyed through the refinery drainage network and is characterized by the potential presence of mineral oils.
- The network of steam acid condensates from the refinery process plants and pretreated by the *soil water strippers*, typically characterized by the presence of ammonia.
- The network of non-recovered steam condensates, not polluted as they have not been in contact with the process (steam under pressure from turbo-machinery, reboiler heating steam, handling lines, storage tanks and instruments).
- Fire-fighting network (hydraulic tests, equipment and exercises).
- Drinking water and meteoric inflows.

Almost all refineries conduct distillation processes in a steam current, with the consequent production of acidic waters characterized by high concentrations of ammonia, hydrogen sulphide and hydrocarbons. These waters have to be subjected to stripping before being conveyed to the treatment plant, where there is often a special section for treating oil-tanker ballast water. The treatment plant carries out a succession of treatments which may be subdivided into: mechanical, biological and chemical-physical. Mechanical treatments (screening, sedimentation, flotation, centrifuging and filtration) remove substances in suspension and floating materials (oils, grease, foam); water/oil gravity separators are particularly important. To increase the effectiveness of de-oiling additional treatments may be foreseen, such as filtration and, above all, flotation with dissolved air in the presence of chemical flocculants. Biological treatments remove organic biodegradable substances generally by means of aerobic processes. It is also possible, using biological methods, to remove nitrogen by means of the biological oxidation of ammonium nitrogen (nitrification) followed by the biochemical reduction of nitrogen compounds oxidized into gaseous nitrogen (de-nitrification). Microorganisms which operate in biological treatment reactors may occur in the form of bioflocs suspended in the water to be treated (activated sludge processes), or may adhere, in the form of a biological film, to inert surfaces (percolated filters, biodiscs, submerged biofilters). Among the main chemical-physical treatments are adsorption on activated carbon, neutralization, chemical oxidation, chemical reduction, ionic exchange, and operations with membranes. Sludges from the ET unit of a refinery generally have to be subjected to various treatments (dehydration, biological or chemical stabilization, desiccation and incineration) prior to their final disposal.

Regarding aspects connected with water consumption and treatment, the refineries adopt an integrated water management system, forming part of the more general environmental management system, with the following aims:

- Reuse of water within the processes, minimization of fresh water consumption, increasing the recirculation thereof, application of techniques for the reuse of treated effluent whenever technically and economically possible.
- Reduction of pollution of waters coming from the single units.
- Separate treatment of particular critical flows (e.g. waters rich in aromatic compounds) before they are conveyed to the effluent treatment plant, to avoid the mixing of particularly polluted flows and to enable the product to be recovered.
- An integrated analysis of the possibility of optimizing the water network and the various users, targeted on reducing consumption.
- Application of techniques to reduce the quantity of effluent generated in each single process, activity or productive unit.
- Collection of wash waters from polluted areas and conveyance to the treatment plant.
- Optimization of the effluent treatment plant.

In particular, in relation to water supply, the environmental analysis should take into consideration: water offtakes from rivers or the sea for industrial use and for cooling plants; the use of drinking water taken from a supply line; the reuse and recovery of treated waters for internal uses (fire-fighting, desalination).

For the purpose of monitoring environmental aspects correlated with water use, the following performance indicators could be found useful:

- Water recovery index: this expresses the reuse percentage of effluents treated for industrial use, with the consequent reduction of offtakes from water supply lines.
- Seawater intake index: this expresses the quantity in m^3 of seawater taken in for cooling purposes, out of the total used expressed in tonnes per annum.

Regarding the management of water discharges, on the other hand, the significant environmental aspects concern: flows or loads to the ET unit (under anomalous or emergency conditions) from refinery plants and/or areas, effluent discharges into surface water bodies from the lines of the ET unit (biological and chemical-physical), the possible discharge into the sea of cooling waters. In order to monitor the significant environmental aspects of the refinery in relation to the management of water discharges, the *discharge conformity index* is useful as a performance indicator. Referred to a particular discharge quality parameter, this index is equal to the ratio, expressed as a percentage, between the value of the parameter in the discharge considered and the legal limit (e.g. if the legal limit is a concentration of 100 ppm and the value of the discharge is 20 ppm, the conformity index is 20%). The lower the conformity index, the better the treatment of the discharges.

9.2.5 Waste management

Soil contamination is generally a lesser problem for a refinery than air and water contamination. Above all, in the past refining processes could have led to spillage on land which now requires reclamation. Pollution is mostly due to dangerous wastes (waste production in a refinery has been estimated as 0.01-2 kg/t of crude treated, 80% being considered dangerous; EIPPCB, 2003), spent catalysts, coal dust, reservoir dregs and sludge from treatment processes, and can be a result of losses, accidents and leaks during transport. There are numerous refinery activities that can generate waste, in particular following: *a*) maintenance operations on plants and tanks; *b*) treatment of discharge waters (with the consequent production of sludges for disposal); *c*) demolition of obsolete plants and building structures; *d*) decommissioning of plants and emptying of reactors (for replacement of spent catalysts).

The management policy of refinery wastes must aim to protect the environment, minimizing the impact of activities and products, and maximizing the recycling and suitable disposal of waste. For this purpose, it is essential to carry out a differentiated collection of the special wastes produced in the various sectors or areas of the refinery, to facilitate recovery, reuse or recycling externally. The main commodity categories of waste collected in a differentiated manner in the refinery are: *a*) inert material not soiled by hydrocarbons (rags, rubber, insulating material, etc.); *b*) oily sludges, dregs, waste resulting from cleaning and reclaiming of plants and/or tanks or reservoirs; *c*) spoil material from excavations, dredging or demolitions (polluted or not polluted); *d*) sludges obtained from treating effluent (centrifuged before being conveyed to the dumping area); *e*) glass; *f*) paper and cardboard; *g*) insulating material contaminated by asbestos, asbestine materials or rockwool; *h*) spent reactor catalysts and filling; *i*) used batteries; *l*) spent oils; *m*) mercury and ferrous wastes, used electric cables, scrap brass.

The procedures that can be adopted for correct waste management are:

- As an integral part of the overall environmental management system, a management system targeted on reducing the production of waste and on preventing soil contamination.
- Optimizing waste collection, sorting and grouping.
- Reducing, during normal operation, the generation of dregs in tanks for crude and heavy products.
- Reduction of waste production during maintenance operations or periods when crude and heavy product tanks are out of service.
- Reduction of the volumes of sludge produced by means of de-watering and de-oiling by centrifuging, using press filters, pressure filters, vacuum rotary filters and disc centrifuges (often these operations are performed with fixed or mobile equipment supplied by specialized companies).
- Closed-circuit sampling systems to avoid dispersion of the product to be sampled.
- Drainage systems and procedures, with the use of dedicated apparatus, containers and tanks, to maximize oil/water separation, reducing the amount of oil placed in the drainage system.
- Procedures and techniques to identify and control the cause of any anomalous presence of oil in the waste water treatment systems.
- Procedures to identify in good time any losses from pipes, reservoirs/tanks and drainage systems.
- The correct management of catalysts to ensure the optimal operating cycle, preventing early disactivation and the consequent production of waste, and checking the possibility of reusing the spent catalyst.
- Optimizing working processes in plants so as to reduce the production of non-standard products and waste to be recycled.
- Optimizing and controlling the use of lubricating oils in machinery so as to reduce the necessity and

frequency of changing parts, and relative production of wastes.

- Carrying out operations regarding the cleaning, washing and assembly of equipment only in dedicated areas constructed for the purpose.
- Optimizing the use of soda in the various product treatment processes (therefore increasing recycling), to be certain that it is completely spent (and no longer fit for process requirements) before being considered a waste.
- Treatment of clay and sand filters and of catalysts with steam before disposal.
- The definition and use of procedures for reducing the entry of solid particles into the drainage network.
- Where possible, the separation of process effluents and rainwater.
- The carrying out of an environmental risk analysis to identify and prevent cases of accidental product spillage; according to the results of this risk analysis, and selectively, the preparation of a timetable of possible corrective measures and actions.
- Minimizing the use of buried pipes, above all for new constructions (this could seldom be applicable to existing plants).
- The installation of a double wall for buried tanks.
- The carrying out of procedures for mechanical inspection, monitoring of corrosion, repair and replacement of worn pipes and of tank bottoms, and the installation of cathodic protections.

In order to monitor the significant environmental aspects correlated with waste management, it is useful to have recourse to the waste recovery index, equal to the percentage of wastes recovered of the total amount produced.

9.2.6 Management of raw materials, finished products and energy

Many petroleum products intended for commercial use are classified as ‘dangerous’ for transport overland, by road or rail (e.g. LPG, gasolines, kerosene, gas-oil and fuel oil). In relation to the management of raw materials and finished products, the aspects that can have important environmental repercussions, either negative or positive, are: *a*) external transportation by sea and by land (with tank trucks) of raw materials, additives, chemicals and finished products; *b*) presence (and the possible release under emergency conditions) of dangerous or inflammable substances in a liquid state, stored in dedicated tanks/reservoirs; *c*) recovery of raw materials during the refining process, such as condensate, slops and liquid sulphur; *d*) realisation of products considered ecological due to the minimum content of polluting substances, such as gas-oil with a low sulphur content and gasoline with a low content of benzene and aromatics.

To monitor the significant environmental aspects of a refinery linked with the management of raw materials and finished products, the following performance indicators are often adopted: the raw materials recovery index, equal to the percentage of losses (water from raw materials, diffuse emissions, gas flares, sludge from treatment of effluents, residues in tanks/reservoirs) of the global balance of the refinery, calculated monthly as a function of the refinery incomings and outgoings; the H_2S to sulphur conversion index equal to the Claus plant conversion percentage; the sulphur recovery index, which expresses the yield of the sulphur recovery activities, calculated annually as a function of the quantity of sulphur in the ingoing raw materials, compared with the outgoing products and the recovery efficiency of the Claus plant.

The improvement in energy efficiency in the various processes reduces the consumption of fuels with a direct effect on the reduction of all emissions into the atmosphere. Among the BAT which aim to improve energy efficiency are:

- The optimal management of combustion operations, recourse to analytic campaigns and periodic controls for improving combustion, the adoption of an energy management system as part of the overall environmental management system.
- Optimizing heat recovery, by studying and effecting the maximization of the heat recovery of hot flows in a single plant, or through thermal integration of a number of plants. For this purpose, over the last few years, considerable progress has been made in designing the systems in such a way as to find the best balance between the investments required for thermal integration and the savings achieved through heat recovery. In particular the method known as *pinch analysis* (Linhoff and Flower, 1978; Smith, 2000) has proved to be a viable instrument for these purposes. Whenever possible it is useful, from the standpoint of energy saving, to recover heat from products coming from the distillation plant, conveying them while hot directly to the other process units downstream of distillation. This is obviously more effective that first cooling the products for storage and then sending them to the other process units. It is also clear that every energy-saving action will also have a positive impact on the environment, because by reducing the thermal burden on the furnace, emissions are also reduced.

- Assessment of the feasibility of applying efficient energy-production techniques, such as using gas turbines with heat recovery boilers, preheating combustion air, installing combined-cycle power generation/cogeneration plants, replacement of inefficient boilers and furnaces with others designed and operating efficiently. For these measures, the following should be examined: technical feasibility within the framework of the refinery's operative and productive configuration, the dimensions of the new equipment and the spaces necessary for installation, the remaining duration of the investment, the effective increase in energy efficiency and the corresponding reduction in emissions obtainable.
- Optimizing heat transfer and thermal recovery in the train of exchangers, for preheating the crude, also by means of using specific 'anti-dirtying' products in the exchangers, in the furnaces and in the boilers. In many cases, these products also lengthen the operative cycle of the exchangers, preventing deposits and blockages in the exchanger pipes, reducing head and pressure losses, and at the same time improving the service factor of the various exchangers.
- The reuse of condensate water.
- Using the flare only during start-up and shut-down operations in emergency situations.
- Optimizing furnace operations, and hence combustion efficiency, through a technically advanced control of the different operative variables (such as the air/fuel ratio). Continuous monitoring of the temperature and the oxygen in the flue-gases should be regarded as the BAT for combustion: furnaces and boilers can in fact typically reach 85% higher thermal efficiency; if preheating of the combustion air is applied and/or the outlet temperature of the flue-gases is kept at a level near to that of the condensation starting point, thermal efficiency could reach levels of 90-93%.

9.2.7 Monitoring

In view of the complexity of refineries in terms of both plants and products used, essential element for proper environmental management is an adequate monitoring system for controlling emissions. The single refineries therefore use, in relation to the specific nature of their management systems, particular procedures for determining, managing, controlling and documenting the data on emissions.

Monitoring of operations and of the emissions produced is fundamental in controlling the operations of the single units, the emissions produced and the results achieved, and for carrying out any corrective actions that might be necessary, for ensuring that legal limits and conformity with environmental audits and checks are respected, and for selecting or planning techniques to improve the environmental performance. A monitoring system therefore has to provide accurate, valid results, as such information forms the basis for reaching the correct operational and technical decisions, and avoiding mistaken or inadequate solutions. Monitoring should be performed during the initial plant start-up activities, during ordinary operations and during interruptions or in anomalous conditions.

In terms of the methodology adopted, the monitoring feasible in a refinery can be: *a*) directly and continuously instrumental in relation to the parameter concerned, by means of analysers installed on the smokestacks through sampling and line analysis (the use of this technique is recommended in cases where there are considerable volumetric flows associated with large-scale variations in the concentration levels of the contaminants present); *b*) indirect, through the correlation between certain continuously controlled chemical-physical process parameters and the emissions associated with them (this technique, too, is widely adopted in cases of high or low volumetric flows associated with the variability of the contaminant concentrations); *c*) directly instrumental of discontinuous type, normally effected through periodic measurements on a reduced time basis (e.g. laboratory analyses of samples taken at the smokestacks), for occasional verifications of emissions that vary very little; *d*) indirect, based on the use of emission factors (this is a form of indirect control often used *ex post* for techniques of final assessment).

Each of these systems involves technical, management and cost advantages and disadvantages. A system is therefore adopted depending on the specific case or plant situation, and bearing in mind the real environmental risk in the territory resulting from the emission of the specific contaminant. Continuous monitoring is not necessarily always more reliable and more accurate than other techniques. In fact, there are many factors, conditions and situations in terms of the plant itself, installation and management, that make the continuous use of analysers particularly delicate, as these require constant specialist maintenance, calibration, cleaning and validation. In establishments with many units, such as refineries, a monitoring system based on a combination of the above-mentioned techniques is frequently adopted (see below for a brief description).

Continuous monitoring. This is typically adopted for units in which the considerable amount of gaseous effluents (flue-gases) and the consequent emissions fluctuate greatly, following hardly predictable qualitative and quantitative variations in the fuels used or in the load. This approach is used, for example, for measuring concentrations of SO_x, NO_x and powders in combustion plants with a rated thermal capacity of more than 300 MW. Continuous monitoring can also be considered, as an alternative to indirect monitoring through correlation, for FCCUs or for Claus plants, which also comply with the above-mentioned general criterion.

Indirect monitoring. This is based on the continuous instrumental measurement of one or more chemical-physical process parameters to which it is possible, with the requisite repetition, accuracy and precision, to correlate the value of the parameter to be controlled. In a process unit, in fact, a series of parameters such as temperature, pressure, flue-gas load, density and composition of products and flows are generally monitored. These data, together with those regarding the composition and quality of the fuels used, are well correlated with the concentrations and quantities of the contaminants emitted. Indirect monitoring, if the software used is accurate, reliable, appropriate for the specific plant condition and borne out by periodic plant data and checks, reaches a degree of accuracy comparable with that of continuous monitoring. Moreover, there are also benefits; this method does not involve problems related to analysers being out of service or becoming dirty, and nor does it entail frequent calibrations and maintenance. Obviously the indirect system is particularly useful and appropriate when applied to those process units in which the data collected are adequate and accurate. A viable application of the indirect system is that of monitoring the emissions of flue-gases from the smokestacks of combustion plants, correlating them with the quality and quantity of the fuel burnt. For example, the sulphur content of the fuel (which can easily be obtained fairly accurately through laboratory analysis) and the quantity of fuel burnt are indicators of the total emissions of SO_x and are at least as accurate as any other continuous monitoring system.

Discontinuous instrumental monitoring. This is used for occasional verifications of emissions which are substantially not very variable, which are of such an amount as to contribute only marginally towards emissions from the whole plant, not producing any significant local environmental effects or, lastly, which are of such a small amount that measurements obtained by specialized personnel through *ad hoc* campaigns based on accurate sampling and laboratory analyses are more reliable.

Indirect monitoring based on factors of emission. It is also possible to utilize emission factors, if borne out by campaigns of non-continuous measurements and agreed with the competent authorities. In this case the quantities of contaminants are determined by multiplying the concentration of contaminants by the volume of the flue-gases, which is in turn calculated using the typical CORINAIR formula (COoRdinated INformation AIR; EMEP/CORINAIR, 2002), or derived from appropriate tables.

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