Pollution Prevention and Control Procedure Case Study: An Application for Petroleum Refineries

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ABSTRACT
There is global environmental concern about the pollution from industries and other organizations that should not only be controlled but also prevented. Many alternatives are available to those in charge of environmental protection, but they should be able to draw on a systematic procedure to help implement prevention and control measures.

At present, there are three immediate tasks: defining the objective of any environmental study, identifying the potential pollution sources, and selecting alternatives to these sources. However, it is necessary to evaluate these alternatives by using as large a number of criteria as possible and making them cumulative so as to enable the classification and selection of the best available techniques for each pollution source.

The petroleum refining industry plays an important role in the developed economies and also has a potential for pollution generation that must be controlled. The best solution for all (i.e., petroleum companies, the public, and the environment) is pollution prevention, because this option will protect all of them and will also reduce costs in terms of lower raw materials consumption as well as reducing potential fines.

IMPLICATIONS
This paper aims to provide a tool for public authorities charged with translating laws from paper into reality. A systematic procedure has been described that can help industries meet the environmental challenges that sooner or later they will be required to face. The method contained in this article makes it possible to develop an ordered, step-by-step procedure regardless of the industry under consideration. The final objective is to find the option by using a broad range of criteria to see the whole picture of the environmental problem.

The procedure we have presented in this article has been applied successfully.

INTRODUCTION
During the last years of the 20th century, environmental authorities from the most developed countries initiated a process to improve environmental protection. Several special environmental policies were consequently implemented with two main objectives: (1) to improve global pollution control, avoiding pollutants transfer between media (air, water, and land); and (2) to enhance the importance of prevention as the best way to protect the environment.

In the United States this effort led to the passing of the Pollution Prevention Act. The act established a hierarchy between the different options to reduce pollution (source reduction, recycling, and treatment), and considered safe waste disposal as the least preferable method. This act also established a program to encourage industry and public organizations to join voluntary programs to prevent pollution generation. The Maximum Achievable Control Technology (MACT) standards also included several provisions aimed at promoting the use of pollution prevention principles. They also included benefits for industry and public organizations when selecting these pollution prevention options that complies with the fixed schedules.

European Union efforts resulted in the European Directive 96/61/European Commission, commonly known as the Integrated Pollution Prevention and Control Directive. This policy established the need for stricter environmental control to provide greater protection for the environment. To achieve this goal the directive strongly recommended pollution prevention options rather than traditional approaches, such as pollutant treatment. This policy required nearly all industrial operators to hold an environmental operating permit based on Best Available
Techniques (BATs). A full definition and description of this concept can be found in the directive text.²

Whereas the European policy is only focused on industry, U.S. policy appeals to all potential polluters (especially those in the public sector) to join their programs. In many instances, the public sector has led pollution prevention initiatives, with industry utilizing those alternatives that clearly yielded a rapid return on investment.

In addition, the European document was intended to serve as an essential guide to the development of suitable solutions for all pollutant generators, whereas the U.S. version offers the pollutant generator more flexibility. This difference between the two policies is a consequence of the fact that the issuing bodies have a very distinct nature: the United States is a single country, whereas the European Union is a conglomerate of many countries.

In both cases, industry or public organizations frequently face very complex situations when upgrading their environmental behaviors, and on many occasions they require a suitable strategy specifically adapted to each particular aim. Pollution prevention requires positive management, some changes in culture, and a systematic approach to understanding what specific releases are occurring to formulate suitable strategies for reducing these through pollution prevention options and to consider potentially competing secondary effects through a proper assessment of needs.

This paper presents a step-by-step procedure to address and resolve such challenges.

METHODOLOGY

The procedure described herein is based on the technique concept, which is defined as the combination of a technology and its operating guidelines. The starting point of the whole process is the use of BATs to prevent pollution or, alternatively, to control it.

As noted above, BAT is not a new concept and has been widely discussed in technical literature.³,⁴ Several advantages and disadvantages arising from these studies can be highlighted.

Advantages of BATs

**Economic Advantages.** Cost reductions from the transport, treatment, and disposal of pollutants, and so forth, lead to a consequent reduction in overall expenses when using this procedure. Improvement in process efficiency results in less raw material consumption. Insurance costs are also reduced. A specific economic analysis for each case, taking into account its individual characteristics, is also provided in this article.

**Legal Advantages.** There are fewer legal responsibilities and associated costs, such as fees and other penalties.

Often laws provide some kind of incentive, as has previously been mentioned in this article when referring to MACT standards, and the benefits that result from a longer time frame for implementing a pollution prevention strategy ensure, for instance, a reduction in atmospheric releases.

**Social Advantages.** Implementation of BATs can help to improve the public image of the industry and/or organization.

**Disadvantages of BATs**

**Economic Disadvantages.** It is difficult to demonstrate the economic benefits associated with BATs. It is not easy to make a detailed breakdown of the associated overhead costs, which usually include environmental ones. Costs and benefits cannot always be assigned or defined globally or universally. Often, the benefits are site-specific and take some time to become apparent.

**Legal Disadvantages.** Policies should include economic incentives to help organizations in their environmental protection efforts.

**Technological Disadvantages.** Because of the lack of reliable information, the impact of pollution reduction measures is usually difficult to predict, whereas production and product quality are commonly the primary concerns for companies in general. Because of its nature, pollution prevention involves emerging technologies or alternative views of processing, of which the efficacy is not yet completely demonstrated for the subject application. So, an element of risk or trial may indeed exist when implementing the pollution prevention strategy.

**Corporate Disadvantages.** BAT implementation leads to changes in the organizational culture.

The difficulty arises when trying to apply a standard procedure to BATs in a particular case. Figure 1 shows a decision flowchart for proceeding through any situation requiring changes. The main obstacle shows up when the staff involved in environmental decisions reaches a point when solving one of these problems requires them to choose a solution from several alternatives. Pollution prevention goes well beyond strictly environmental issues, and it is necessary that process personnel participate in the stages included in Figure 1.

Although such decision-making approaches have been previously reported, they often require a full knowledge of a complex methodology⁵ or a very detailed list of pollutants to obtain reliable results.⁶
The third stage is identifying problems and establishing priorities. By developing a precise understanding of the causes of pollutant generation, it is possible to choose the right solution from a range of technical alternatives. Usually, this is not an easy task, and more than one alternative will be required.

**Determining Remedial Solutions.** Once the priorities have been established, the next step is the determination of the most suitable remedial solutions. There will probably be many alternatives for each of the priority problems. The appropriate solutions in each case can be selected from references in technical literature that offer proven solutions from previous similar experiences. It is also possible to select options with a greater degree of risk in terms of innovation.

**Solution Analysis.** It is important to develop a procedure to rate different alternatives for the prevention and/or control of pollution generation. A critical point is this respect is the rating of each environmental alternative using different criteria to obtain the whole picture, which includes the advantages and disadvantages of the different alternatives. These criteria can be grouped into four categories: risk, environmental, technical, and economic criteria. These have been chosen to cover all the key aspects of the American and European policies.

**Risk Criterion**

**Risk Reduction.** Risks, especially to human health, should be given special consideration when referring to emissions of carcinogenic and lethal chemical species, such as H₂S or benzene, even when they occur at low concentrations.

**Technical Criteria**

**Raw Material Use.** The criteria includes optimization of raw material consumption by increasing process efficiency.

**Applicability.** Previous satisfactory experience with a particular BAT and the scope for its application not only to similar factories but also to any other industry or organization is a part of the criteria.

**Time Consumption.** The time required to apply the BAT in question must also be included. Usually, industries take advantage of planned shutdowns to incorporate...
Environmental protection measures. The possibility of incorporating a BAT on-stream, with no shutdown required, should be considered. The time necessary to implement a BAT is the time needed not only to install the equipment but also for the training of personnel in the implementation of the new BAT. This last comment is particularly important when talking about procedural changes or new work practices.

**Environmental Criteria**

*Control Efficiency.* Criteria include determining the reduction percentage achieved according to base values (i.e., noncontrolled pollution values).

*Environmental Hierarchy.* Hierarchies both from the legislation and from literature are as follows: source reduction, recycling (both internal and external), waste treatment, and safe disposal.

*Reduction of Pollutants.* The number of pollutants should be reduced using a particular BAT. Examples from a petroleum refinery include the following: atmospheric emissions (sulfur dioxide [SO₂], nitric oxides [NOₓ], volatile organic compound [VOC], CO, and particulates), wastewater (storm water, wastewater from processes, and utilities such as boiler feed water and cooling water), and wastes (spent caustic, oily sludge, and spent catalysts).

*Byproducts and Waste Generation.* Application of the BAT should avoid the formation of byproducts to prevent pollutant transfer from one medium to another.

*Total Amount of Pollutant Reduction.* This criterion combines two aspects: efficiency control of the BAT over the pollutant source and relative wt of this source over the total amount of that pollutant.

**Cost Criteria**

*Investment.* The required investment for chemicals or equipment and its installation should be included.

*Operation and Maintenance (O&M) Cost.* Cost associated with the O&M of the BAT should be considered.

*Unitary Cost.* The ratio of total annual cost and rate of pollutants should be reduced.

When using different evaluation criteria, it is difficult to sum up each criterion to obtain the whole picture for each BAT. This can be solved with the following two-step procedure.

Each BAT should be evaluated independently with respect to each of the criteria used. This should be the case even where some of the criteria are rated using a qualitative scale and others a quantitative scale.

Each criterion rating scale shall be standardized as follows: the best environmental level of the scale shall be rated as five points and the worst environmental level as one point.

Table 1 shows the two above-mentioned scales for each criterion. This table has been prepared by the authors but can be modified following a case-by-case analysis. A different number of criteria can be included, as well as a different way of rating for these criteria.

*Selecting the Most Suitable BAT.* The last step is to make a ranking based on the sum of all of the partial scores for each criterion to obtain the total score as shown in eq 1.

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**Table 1.** Score assignment for each criteria.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Risk reduction</td>
<td>Very low</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>Very high</td>
</tr>
<tr>
<td>Raw material usage</td>
<td>Increase consumption</td>
<td>Low</td>
<td>—</td>
<td>No change</td>
<td>—</td>
</tr>
<tr>
<td>Applicability</td>
<td>R&amp;D degree</td>
<td>Commercial without references</td>
<td>—</td>
<td>Particular for each factory</td>
<td>Industry specific</td>
</tr>
<tr>
<td>Time required for implementation, years</td>
<td>7+</td>
<td>5-7</td>
<td>3-5</td>
<td>3-1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Efficiency control (%),</td>
<td>&lt;15</td>
<td>15-40</td>
<td>40-70</td>
<td>70-95</td>
<td>95+</td>
</tr>
<tr>
<td>Environmental Hierarchy</td>
<td>Safe disposal</td>
<td>Treatment</td>
<td>External recycle</td>
<td>Internal recycle</td>
<td>Source reduction</td>
</tr>
<tr>
<td>Pollutants reduced</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4+</td>
</tr>
<tr>
<td>Byproducts and wastes produced</td>
<td>Very high</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>Very low</td>
</tr>
<tr>
<td>Total amount pollutant reduction (%)</td>
<td>&lt;10</td>
<td>10-30</td>
<td>30-60</td>
<td>60-80</td>
<td>80+</td>
</tr>
<tr>
<td>Investment</td>
<td>Very high</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>Very low</td>
</tr>
<tr>
<td>Operation and maintenance costs</td>
<td>Very high</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>Very low</td>
</tr>
<tr>
<td>Unitary cost</td>
<td>Very high</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>Very low</td>
</tr>
</tbody>
</table>
where $x_i$ is the relative weighting of each criterion with respect to the remaining criteria. Throughout the explanation of the procedure, it has been assumed that each of the criteria is equally weighted, but when applying this methodology to a particular case, some criteria may be given more importance than others. Furthermore, new criteria can be added to the proposed list, in addition to or replacing any of them. Corporate goals that are site-specific could be an example of this, because the particular goals of institutions or industries can differ from each other. The usefulness of the procedure comes from the ability to adjust both relative weighting and criteria to the needs of each situation that it provides. This option to adjust the relative weighting is also included in the Figure 1 flowchart. Additionally, $y_1$ refers to the score for each criterion, as given in Table 1. This procedure rapidly provides the whole picture for any BAT along with its advantages and disadvantages. It is not meant to be a static procedure; it can be changed, either to add or substitute criteria to better adapt it to particular situations or to give special relevance to a specific criterion.

**CASE STUDY: AN APPLICATION FOR PETROLEUM REFINERIES**

Petroleum refineries are big industrial complexes configured by unit operations that are required to manufacture a range of commercial products from crude petroleum. These products range from liquefied petroleum gases (LPG), gasoline, kerosene, and diesel to specialized products such as lubes, solvents, petrochemical feedstock, sulfur, and waxes.

The example of the petroleum refinery makes for a very interesting analysis because of the refineries’ complexity and the large number of unit operations they all have. Several of those unit operations are common to other industries, whereas others are very specific to this industry.\(^7\)

In addition, petroleum refineries have the capacity to manufacture a huge number of different commercial products. Thus, we should also consider the different nature of the feed (petroleum crude). As a consequence of this, experts usually affirm that there are no two identical refineries. That implies that each refinery requires a particular study.

Refineries from developed countries share one feature, that is, their conversion degree. The conversion degree is defined as the capacity to convert a barrel of crude into commercial products with a higher economic value, that is, gasoline, kerosene, and diesel. Most modern refineries have a medium-to-high degree of conversion.

Distillation, absorption and adsorption, chemical reaction, extraction with solvents, and so forth are the unit operations that make up a refinery operation. They consume a huge amount of water, energy, catalysts, and chemicals.

As a result, the following environmental issues may be expected. Atmospheric emissions may be expected mainly because of combustion products (in terms of the greatest mass of emissions) but also because of the storage tank farm and the sulfur recovery plant. Wastewater may be expected because of the number of processes in a refinery requiring large volumes of water. Additionally, solid wastes may be expected because of off-specification process streams, spent catalysts, and spent caustics.

Because of the many pollution sources in petroleum refineries, it is necessary to determine the most important ones.

**Atmospheric Emissions**

Petroleum refineries are important generators of the following pollutants: $SO_2$, $NO_x$ (NO and $NO_2$), VOC, CO, and to a lesser extent $NH_3$, $H_2S$ and particulates. Sources for these pollutants are listed below.

**Combustion Processes.** The pollutants generated in combustion processes represent 80% of the total main pollutants ($SO_2$, $NO_x$, and particulates) and are present in most unit operations. It is worth noting that a medium-to-high conversion refinery spends 9% of the crude fed to the complex as fuel for combustion processes.

**Fluid Catalytic Cracking Unit (FCCU).** This unit converts heavy gas-oil into more valuable products (LPG, gasoline, and light gas-oil); it is an important source of $SO_2$, $NO_x$, and particulate emissions.

**Storage of Feedstocks and Products.** Storage of feedstocks and products are thought to be one of the most important sources of VOC emissions in the refinery.

**Liquid Effluents**

Main contributors of liquid effluents are as follows.

**Crude Desalter.** Crude composition includes inorganic salts that need to be removed before processing. To attain this objective, crude is washed with fresh water before crude atmospheric distillation. The resulting aqueous effluent has high organic (because of oil entrainment) and inorganic loads.
FCCU and Hydrotreating Processes. The process of making up water to prevent inorganic salt formation in heat exchangers produces liquid effluent with high levels of H$_2$S and NH$_3$.

Utilities Systems. Every refinery, as any other chemical industrial complex, has a network of utilities. Among them, the cooling water and boiler feed water systems need a blowdown stream, which contains a high level of solids and chemicals.

Solid Wastes
Solid wastes that should be taken into account as part of total waste generation are as follows.

Process Purges. Different process units throughout the refinery produce streams that are out of specification (because of process malfunction or maintenance reasons), which need to be managed either internally or off-site.

Catalytic Units. Many of the process units need to be operated with catalyst support. This requires spent catalyst to be properly managed.

Caustic Treating Processes. Sulfur species with corrosive properties need to be removed using caustic solutions (10% wt concentration typical) to produce commercial products (LPG and light gasoline). Spent caustic streams need to be managed to reduce their high chemical oxygen demand (COD).

Because of the configuration of the units, most of them can be a potential source of pollutant to more than one media. For example, the FCCU generates wastewater that needs to be treated before reusing or discharging it to a river, in addition to the considerable atmospheric emissions that it generates.

A review of specialized publications shows a great number of alternatives that can be implemented to prevent and control pollution from the processes listed above. This article proposes a systematic procedure that enables the reader to evaluate these alternatives.

The environmental alternatives to be analyzed in the article include the following: (1) NO$_x$ emissions, reduction of NO$_x$ emissions from combustion processes; (2) liquid effluents, reduction of wastewater generation; and (3) wastes, minimization of oily sludge and spent caustic.

BATs for Minimization of NO$_x$ Emissions from Combustion Processes
The proposed BATs to be analyzed are as follows: (1) low NO$_x$ burners, (2) use of gaseous fuel, (3) selective catalytic reduction, and (4) energy integration.

Combustion NO$_x$ is mainly attributed to fuel NO$_x$ (from the nitrogen in the fuel) and thermal NO$_x$, meaning that generated through oxidation of nitrogen at high temperature. These two sources of combustion NO$_x$ lead directly to the first two proposed BATs. The second BAT is a post-treatment of the combustion gases, and the last BAT aims to produce a source reduction through a reduction in fuel consumption.

Low NO$_x$ Burners. Nowadays industries install low NO$_x$ burners to reduce thermal NO$_x$ generation by achieving lower flame temperatures. The main types of technologies being used involve either air or fuel staged addition. Some gas burners incorporate flue gas recirculation as an alternative to reduce flame temperature.

Selective Catalytic Reduction. This is a proven technology that favors the reaction of combustion gases (including NO$_x$) with added NH$_3$ (supported by V$_2$O$_5$/TiO$_2$ catalyst). The main reactions that take place include the following:

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]  
\[ 4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \]

The presence of a catalyst enhances the reaction, lowering operating temperatures down to a range between 315 °C and 400 °C.

Use of Gaseous Fuels. Substitution of conventional liquid (nitrogen-containing) fuels with gaseous fuel (nearly nitrogen-free) significantly reduces NO$_x$ emissions; natural gas produces 159 mg/Nm$^3$ versus fuel oil production of 350 mg/Nm$^3$. In addition, there is a significant reduction in other atmospheric pollutants such as SO$_2$ (natural gas can be assumed to have a negligible sulfur content), particulate, and CO/CO$_2$.

To include this BAT in an industry is not always a straightforward task. It requires the full involvement of a planning team, and it is necessary to make an individualized economic assessment.

Key issues for consideration during this analysis are the following: (1) the need to burn fuel gas produced throughout the refinery, and (2) the need to burn residual liquid fuels that do not comply with commercial specifications.

Twenty-first century refineries need to minimize heavy fuel production, especially residual fuels mentioned in the previous point. Moving away from heavier fuels reduces the amount of waste disposal required. There is a downside, however; often the cleaner fuels are more costly to use than the heavier fuels that would be readily available at a petroleum refinery.
Energy Integration. Several energy integration techniques, such as Pinch Technology, help refiners to optimize their fuel consumption and, consequently, their atmospheric emissions. A typical application is a heat exchanger network or integration of a reboiler and condenser into the same heat exchanger. An energy integration plan for a 700 m$^3$/hr crude distillation unit can produce an annual financial saving of U.S.$700,000 because of the 684 kg/hr of non-burnt fuel (5470 mT/yr with an on-stream operating factor of 8000 hr/yr). This energy integration plan also produces an important reduction in atmospheric pollutants: (1) SO$_2$: 14.5 kg/hr, considering that sulfur fuel oil content is 2% wt, (2) NO$_x$: 4.2 kg/hr, (3) CO$_2$: 2134 kg/hr, and (4) particulate matter: 0.9 kg/hr.

**BATs to Reduce Liquid Effluents**

The proposed BATs to be analyzed are the following: (1) integration of different water consuming processes, (2) liquid stream segregation, and (3) reverse osmosis units.

Integration of Different Water Consuming Processes. There are two objectives of water integration: a reduction in the net amount of water consumed and a reduction in the total loading of pollutants that must be treated in WWTPs (wastewater treatment plants) for final discharge. These objectives can be accomplished by process water, storm water, and cooling water recycling and reutilization, in a two-stage process: (1) water mass balance throughout the refinery and for each process unit, and (2) setting min water feed quality requirements (max values for some pollutants) for each unit and effluent composition analysis.

After completing these two stages to establish the vol and loadings to and from each unit, pollution prevention options applicable to those streams (individually or combined) can be developed. After determining which option(s) will be pursued, objectives can be established, measured, and progress toward the goal/objective monitored.

A previous study on water conservation discussed several options for water consumption optimization and calculated the cost and efficiency of wastewater reduction.

Table 2 includes several options for water conservation. It can be seen that Table 2 contains information that is site-specific because of local factors (specific laws and location of the refinery), as well as economic factors (cost of fresh water and treatment for wastewater).

Some of the limitations for water conservation studies are the following: (1) corrosion phenomena, (2) fouling and sedimentation, (3) loss of mass transfer in washing process using water, and (4) WWTP location in relation to the point of use because of the pumping cost. This can represent an unaffordable financial cost for the refinery.

**Liquid Stream Segregation.** Water consumption optimization can be enhanced with proper stream segregation based on the nature or composition of those streams. An indiscriminate mixture of heavily contaminated aqueous streams with other lightly contaminated streams should be avoided, because any potential for reuse would probably be lost. Advantages of this selective segregation are as follows: (1) lower amount of water to be treated as wastewater, (2) selection of the most appropriate treatment for each stream avoiding unnecessary streams and avoiding dilution of other streams that would increase the difficulty of treatment, and (3) lower initial investment required as well as less operating costs for both water conditioning and water treatment.

**Table 2.** Water consumption integration among different processes.

<table>
<thead>
<tr>
<th>Option</th>
<th>Wastewater Source</th>
<th>Main Pollutants</th>
<th>Selected Treatment</th>
<th>Final Destination</th>
<th>Water Consumption Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process changes</td>
<td>Vacuum ejectors</td>
<td>H$_2$S, H$_2$O, NH$_3$</td>
<td>Use of liquid ring pumps</td>
<td>Wastewater generation expected</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Live steam strippers</td>
<td>H$_2$S, H$_2$O, NH$_3$</td>
<td>Substitution by reboilers</td>
<td>Reduction of wastewater generation</td>
<td>30</td>
</tr>
<tr>
<td>Reuse without regeneration</td>
<td>FCCU, visbreaking, coking (quench stage)</td>
<td>Hydrocarbons, phenols, sulfur</td>
<td>No treatment required</td>
<td>Crude desalters</td>
<td>5</td>
</tr>
<tr>
<td>Reuse with partial regeneration</td>
<td>CDU/VDU, HDT, FCCU, visbreaking, coking (steaming stage)</td>
<td>H$_2$S, H$_2$O, NH$_3$</td>
<td>Sour water stripping</td>
<td>Crude desalters, wash water to remove inorganic salts, water for coking unit</td>
<td>5</td>
</tr>
<tr>
<td>Recycling regenerated water</td>
<td>Refinery</td>
<td>H$_2$O</td>
<td>WWTP</td>
<td>Coking unit make up for cooling water circuit.</td>
<td>5-25</td>
</tr>
</tbody>
</table>

Note: NA = not available.
Rational stream management is based on stream characterization, and classification is as follows: (1) oil-free contamination streams, for example, steam condensate from heat exchangers; (2) accidentally oil-contaminated streams, for example, storm water collected from process areas; and (3) continuously oil-contaminated streams. They can be divided into high organic load streams (wastewater from tank area and crude desalters) and low organic load ones.

Reverse Osmosis (RO) Units. RO units are a real option to improve water consumption in particular cases. Costs have been significantly reduced, and analysis of each case can show positive financial benefits. Typical applications of this are boiler feed water conditioning processes and water quality improvement of WWTP effluent, because it can be considered as a potential feed for the cooling water circuit.

Advantages associated with the use of ROs are easy to evaluate and include a 90% efficiency rate in water pollutants removal, a lower risk of deposits in water coolers, lower sludge generation because of higher quality water, and a reduction in associated treatment. The main disadvantages are the high level of investment required for this and the importance of influent quality (pretreatment usually required).

**BAT for Waste Minimization**

The proposed BATs for waste minimization are described. Oily sludge BATS include the following: (1) integrated sludge management system, (2) tank bottoms minimization, and (3) oily sludge destruction in coking units without pretreatment. Spent caustics BATs include the following: (1) segregation and cascade reuse, and (2) wet air oxidation units.

**Integrated Sludge Management System.** Figure 2 shows a typical integrated scheme for sludge management in a modern refinery. This scheme has been selected by the authors as a candidate to be a BAT for the following reasons: (1) the reduction of solid build-up which otherwise tend to increase sludge generation, and (2) the improvement of oil recovery and its posterior recycling to process units.

**Tank Bottom Minimization.** Minimization of generation of tank bottoms (heavy components that decant during storage time) can be achieved using dedicated emulsifying chemicals. An average composition of sludge tank bottoms may consist of the following: hydrocarbons 40–90%, water 10–50%, and solids 2–50%.

Emulsifiers can help to produce a homogeneous composition in the tank avoiding bottom generation. The main disadvantage is that entrainment emulsifiers can disrupt crude desalter operation. This is the reason why its usage must be carefully analyzed in each particular case.

Other options are available, such as tank design or programmed throughput, but these do not offer the same advantages as emulsifiers in terms of time of implementation and operational flexibility.

**Oily Sludge Destruction in Coking Units Without Pretreatment.** Refineries with coking units in their process scheme can use these to destroy the following oily streams without the need for pretreatment: (1) American Petroleum Institute separator sludge, (2) dissolved air flotation unit sludge, (3) oily residual streams, and (4) sludge from heat exchanger cleaning process.

This operation allows hydrocarbon recovery, whereas solids get trapped inside the coke. The amount of sludge that can be destroyed is controlled by several factors: (1) coke quality: metals, ash, and VOC limit the quality required for commercial sale; (2) 1 kg of sludge per mT of coke production; and (c) max unit capacity: feeding these sludges reduces fresh feed rate.

The main advantages of these BATs are the ability to destroy hazardous wastes without any pretreatment and the cost reduction arising from waste management processes no longer required. The main disadvantages are that this BAT entails a lower level of energy efficiency, a reduced coke quality, and a reduction in distillate production depending on the coke feeding system.

Another point to take into account is the cost and efficiency of the process versus the disposal and beneficial use of a material that would otherwise be handled as a
waste. This is a balance that must be assessed and managed in the light of both economic and process considerations.

Spent Caustics Segregation and Cascade Reuse. The petroleum refining industry removes sulfur acid compounds from petroleum distillates using caustic solutions. Those impurities are mainly H₂S and mercaptanes.

Unfortunately, this kind of chemical treatment generates a significant amount of spent caustics. These wastes cannot be massively fed to WWTP because of their COD values, mainly caused by compounds such as Na₂S, sodium mercaptides, and thiols.

Proper segregation of spent caustics permits their efficient management. The criterion for this segregation is the nature of the pollutants (napthenic, sulfidic, and phenolic) removed during neutralization processes.

As a consequence of this segregation, the spent caustics may be reused in a cascade: spent caustic and distillate streams are mixed cross-currently to improve mass transfer of the pollutants; the spent caustic for one process unit can be reused in other processes that are less demanding in terms of the quality of the caustic. As a result, caustic consumption significantly decreases.

Wet Air Oxidation Units for Spent Caustics. Oxidation of spent caustics with wet air at high pressure and temperature conditions allows refineries to send these caustics to WWTPs because of the COD reduction with values up to 80% and a nearly total destruction of phenols and other heavy sulfur compounds. Typical operating conditions are 270 °C and 100 kN/m².

The main disadvantages, when comparing this with conventional process units, are the high level of investment required and the high operating costs. The degree of investment results from the equipment design conditions (design temperature and pressure, as well as metallurgy), which become necessary on account of the severe operating conditions in terms of pressure, temperature, and corrosive chemical species. High operating costs are incurred on account of the consumption of utilities, mainly high pressure steam and electricity.

RESULTS

The procedure described above has been applied to the case of petroleum refineries. First, for identification of problems and establishment of priorities, several of the most relevant pollution problems in a petroleum refinery have been selected. Second, for fixing remedial solutions, several BATs to prevent or minimize these environmental problems have been proposed. Regarding solution analysis, the proposed BATs have been rated by applying the score assignment guidelines included in Table 1. Each technique has been rated under every criterion, and total scores are obtained by adding partial scores from different criteria ratings. Because this is a general case, an equal-weighting situation has been selected. Fourth, for selection of the most suitable BATs, those total scores produce a whole picture for each analyzed BAT and establish a ranking as shown in Figure 3. Final scores, together with the associated ranking included in Table 3 and Figure 3, must be carefully analyzed and applied, because the procedure must be modified on a case-by-case basis, considering the particularities of each case.

Once this procedure has been applied in a particular case, there are some notable benefits. First is the ability to select the most appropriated BAT on a case-by-case basis among several options: no alternative should be discarded without carrying out an appropriate analysis. Next is proper assignment of economic resources. Economic resources are usually limited. It is, therefore, necessary to establish investment priorities in the light of available resources.
### Table 3. Rating of proposed BAT based on recommended procedure.

<table>
<thead>
<tr>
<th>Criteria Groups</th>
<th>Risks</th>
<th>Technical</th>
<th>Environmental</th>
<th>Economical</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAT</td>
<td>Risk Reduction</td>
<td>Raw Material Use</td>
<td>Timeliness (years)</td>
<td>Applicability</td>
</tr>
<tr>
<td>Low Nox burners</td>
<td>(VL)</td>
<td>(NC)</td>
<td>(3–5)</td>
<td>(AI)</td>
</tr>
<tr>
<td>NOx SCR reduction</td>
<td>(VL)</td>
<td>(NC)</td>
<td>(3–5)</td>
<td>(AI)</td>
</tr>
<tr>
<td>Gaseous fuels</td>
<td>(L)</td>
<td>(NC)</td>
<td>(7+)</td>
<td>(AI)</td>
</tr>
<tr>
<td>Energy integration</td>
<td>(L)</td>
<td>(DC)</td>
<td>(3–5)</td>
<td>(FS)</td>
</tr>
<tr>
<td>Water consumption</td>
<td>(L)</td>
<td>(DC)</td>
<td>(1–3)</td>
<td>(FS)</td>
</tr>
<tr>
<td>Aqueous streams</td>
<td>(M)</td>
<td>(DC)</td>
<td>(5–7)</td>
<td>(IS)</td>
</tr>
<tr>
<td>Segregation</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Reverse osmosis units</td>
<td>(VL)</td>
<td>(DC)</td>
<td>(1–3)</td>
<td>(AI)</td>
</tr>
<tr>
<td>Chemical compounds to minimize bottoms tanks</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Integrated sludge Management system</td>
<td>(VL)</td>
<td>(DC)</td>
<td>(1–3)</td>
<td>(FS)</td>
</tr>
<tr>
<td>Sludge destruction in coking unit</td>
<td>(M)</td>
<td>(DC)</td>
<td>(1–3)</td>
<td>(FS)</td>
</tr>
<tr>
<td>Spent caustic segregation and cascade reuse</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Wet air oxidation units for spent caustics</td>
<td>(L)</td>
<td>(NC)</td>
<td>(5–7)</td>
<td>(AI)</td>
</tr>
</tbody>
</table>

**Notes:** VL = very low; L = low; M = medium; H = high; VH = very high; SR, source reduction; IS = industry specific; FS = particular for each factory; AI = applicable for all industries; DC = decrease consumption; NC = no change.
resources and to prepare a ranking of all BAT options. Both of these steps can assist in making a decision. Last, discovering hidden opportunities and risky options: the proposed procedure can help to discover economic as well as legal benefits that are not obvious or to discard BAT options that imply relevant costs with low environmental results when applied to our case.

CONCLUSIONS

Legal pressure on industries and pressure from organizations urging them to protect and control the environment is growing daily. To comply with this legal pressure, potential polluters should choose not only pollution control but also pollution prevention. There are a huge number of options to achieve this, and it is advisable to adopt a systematic approach to evaluate these procedures. This article describes one such procedure that fits well with this aim, because it allows for the selection of techniques that prevent and control pollution generation.

Petroleum refineries have been chosen as a case study because of their importance in the current modern economy (growing distillates consumption market) and their potential as pollution generators. The main obstacle is not in defining BAT candidates but in selecting the most suitable BATs for a particular refinery.

When selecting from different BAT options, it is important to consider the specific features of each refinery, such as geographical location, the nature of the feedstock and final products, as well as the presence of other industries in the same area.

No BAT should be rejected because of its apparent simplicity or complexity: different BATs could involve the introduction of a modern technology or an inexpensive change in operating procedure. Rating them by the multiple criteria procedure presented in this article, which avoids complicated mathematical calculations, has been found to be an easy and straightforward procedure.

REFERENCES

1. United States Congress. Pollution Prevention Act, PL 101-508, Title VI, subtitle F, Sections 6601-6610; et seq. 1990.

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