# LIFE CYCLE OPTIMIZATION

> Consider the reaction in the U.S. if the Soviet Union were to threaten, as global climate change threatens, to invade 7000 square miles of U.S. coastal land, incapacitate a significant fraction of U.S. agriculture, reduce hydroelectric capacity and degrade water quality in many regions, all in the next 50 years. What level of resources would be committed to stopping this threat?
>
> *Joel N. Swisher (1989)*

The quote above, which was made in reference to a USEPA report on global warming (1), provides the thematic introduction and motivation to this chapter. The environmental problems that have been added to a process engineer's list tend to be more global in scope than ten years ago. In the past, engineers and legislators worried about the effect of stack emissions on the air quality of the cities in which we live. Now, in addition, they must consider the impact of those same emissions (as well as other sources) on the climate and stratospheric ozone layer of the entire planet. Acid rain does not respect international boundaries, and hazardous wastes that are too expensive to dispose of here, all too often wind up halfway across the planet. For these reasons, the early environmental activities that have primarily dealt with treating process waste after its generation (end-of-pipe treatment) are gradually transformed to pollution prevention approaches to achieve economically and environmentally competitive process designs.

The objective of life cycle optimization is to develop a consistent framework to help process engineers, legislative bodies, and environmental agencies identify opportunities for environmental impact minimization in the process industries by considering process technological, material alternatives and their interactions, cost implications for production and scheduling, and input as well as output waste generation due to intentional and unintentional operation in a unified way.

Many articles report successful case studies, and several guides attempt to provide a systematic approach to waste minimization and pollution prevention (2–4). Their approach involves ranking waste minimization alternatives and proposing practical techniques that can be applied to waste generation problems such as technology replacement, source reduction by process changes and equipment modifications, and on/offsite recycling of waste materials.

Process synthesis involves the "act of determining the optimal interconnection of processing units as well as the optimal type and design of the units within a process system" (5). The two basic approaches, which have been established over the last 20 years to address the process synthesis problem, (1) hierarchical decomposition and evolutionary techniques and (2) mathematical programming-based methods, have been extended to account for waste considerations.

## HIERARCHICAL APPROACH FOR WASTE MINIMIZATION

The hierarchical decision procedure described by (6) provides a simple way of identifying potential pollution problems early in the development stages of the design. If these decisions are changed, other process alternatives are generated. Some of the decisions affect the exit streams from (and the feeds to) the process and, in some cases, these exit streams have an adverse environmental impact. Hence, Douglas proposes that if we can make decisions, that is, find alternatives that do not lead to pollution problems, we can develop cleaner processes. Based on such a hierarchical approach, (7) reported on process integration studies for waste minimization. Process improvement options are identified to minimize emissions and waste generation.

Douglas' approach motivated (8) to distinguish between wastes generated in a process, that is, process wastes (produced in reactors, separation systems, and process operations) and utility wastes (associated with hot and cold utilities), and (9) introduced the idea of the Graphical Mass Balance, a visual means of mass balance manipulation which can be used for an initial exploration of the operating conditions of a process in order to meet environmental regulations.

## ENVIRONMENTAL APPLICATIONS OF MATHEMATICAL PROGRAMMING

The concept of mass exchange networks (MENs) has been developed by Manousiouthakis, El-Halwagi, and coworkers (1989, 1990, 1992) to provide a way of configuring a minimum cost separations network which meets environmental discharge constraints. "End-of-pipe" treatment can be integrated with the utilization of waste materials through the synthesis of mass efficient processes. Wang and Smith (10) developed techniques to target and design for minimum wastewater for re-use, regeneration re-use, and regeneration recycling.

The discontinuous nature of many processes poses not only a difficult problem in sequencing and scheduling the tasks to manufacture some products but also in the reduction of waste generation time-dependent profiles. Grau et al. (11) tackled the waste minimization problem in multipurpose batch plants as part of the constrained scheduling problem with limited resources. Pollution indices had been attached to cleaning streams to quantify their environmental impact aiming at the minimization of the product changeover waste. However, throughout their work, the design is considered to be given, and pollution is addressed at a macro scale. Stephanopoulos and his coworkers employed ideas of lexicographic goal programming as a means to generate the pareto curve of solutions so as to incorporate ecological considerations in batch process design. Linninger et al. (12) developed a methodology to design batch processes with Zero Avoidable Pollution (ZAP) by detailed consideration of alternative reaction systems, solvents, catalysts, separation processes, and treatment units. The above ideas have been implemented in an integrated, computer-aided environment, called Batch Design Kit, comprising a physical property and legislation limits database, a batch process synthesizer, and a simulator. The software development has been applied mainly to pharmaceutical processes (12). Another design system for pollution prevention in process and product design is the Clean Process Advisory System, or *CPAS™* (13). It is a product under development by collaboration between industry, academia, and government and includes tool groups such as new technology, pollution prevention design options, treatment design options, technology modelling, industry planning, environmental risk, etc. The combined result will enable engineering designers to come up with environmentally benign conceptual designs. Petrides et al. (14–15) developed a user friendly design kit, EnviroCAD, for deriving alternative waste treatment designs by recommending, based on waste input, options for waste recovery, recycling, and in cases where this is not possible, alternatives to treat or dispose of the wastes generated. Recently, Elliott et al. (16) provided a computer aided implementation of relative environmental impact indices to calculate the deviation of environmental damage associated with a process for different design and operational alternatives.

## RISK ANALYSIS TOOLS

Apart from industrial pollution related to conventional process effluent streams, accidents such as the Seveso incident in Northern Italy highlighted the need to address the impact of such incidents on the environment. For this reason, the European Commission provided the first legislative framework for controlling human hazards called the Seveso Directive. Most of the latest methods for assessing environmental impact of nonroutine releases are simple and qualitative, such as checklists and networks (17). To differentiate from human risk assessment, environmental risk assessment should consider the various components of the environment such as air, water, and soil.

Qualitative hazard identification techniques [for example, hazardous operations (HAZOP)] are currently employed to assess the adverse environmental effects at a post release level (18). Risk related events (like accidents, off-spec. production, etc.) have been incorporated quantitatively in formal environmental impact assessment by Aelion et al. (19) through the idea of the frequency/environmental load curve. In particular, they distinguished release scenarios depending on whether they result from intended or unintended plant operation (e.g., production of off-spec material, disposal of perished material, leakage); an aggregate figure of the annual process environmental load attributed to accidents is represented as a function of the expected number of unintended events per year (frequency) and the environmental load released during each accident.

## LIFE CYCLE ANALYSIS PRINCIPLES

The approaches described above can provide useful results about the waste generation from a process; however, from an environmental viewpoint, they typically overlook an important issue. They provide systematic methods to evaluate the optimal way to cut down waste generation by the process (i.e., to reduce *emissions* waste, but do not take into account the waste associated with *inputs* to the process (such as wastes associated with raw materials and energy generation, capital plant, etc.). Clearly by employing energy to remove mass discharges, process emissions can be reduced; however, it does not necessarily follow that the environmental impact of the process is reduced since the wastes associated with the provision of the energy may outweigh the original emissions problem. In a similar way, higher purity starting materials or improved catalysts may lead to reduced emissions from the process under consideration but may incur a greater overall degree of environmental damage through the raw material purification or catalyst production stages.

Another important point not addressed to date by the waste minimization methodologies is the systematic quantification of the environmental impact of process wastes. Generally, most techniques have been confined to systems in which the environmental impact has been measured in terms of the mass discharge of a single species (e.g., phenolics). In cases where many different kinds of wastes are emitted from a process, any sensible waste minimization approach would need to weigh these emissions in some consistent way.

Some of these issues have been addressed in the field of Life Cycle Analysis (LCA). This is a methodology aimed at quantifying the full range of environmental impacts of a product, and of its material and process inputs, over its complete life cycle, encompassing extraction and processing of raw materials, manufacturing, transportation and distribution, use/re-use/maintenance, recycling, and final disposal. LCA has been used in evaluating eco-labelling and extensive LCAs have been carried out to establish the environmental impacts of various products (20–21). A methodology for performing LCA has been formally defined by the Society for Environmental Toxicology (22) and comprises three stages: (1) preparing a Life Cycle Inventory, which is an inventory of all material and energy requirements associated with each stage of product manufacture, use, and disposal (e.g., to find the impact of VCM, the inventory is based on the system defined in Fig. 1), (2) performing a Life Cycle Impact Analysis, a process in which the effects of the inventory on the environment are assessed, and (3) addressing the Life Cycle Improvement Analysis, which is aimed at reducing the product impact on the environment. Most LCA studies to date have focussed on the inventory component, although there are well developed techniques for performing the Impact Analysis as well (23). Generally, where chemicals manufacturing processes have been included in an LCA (for instance, the production of ethanol for use as a hairspray propellant), the inventory data has been based on industry standard practice and has not been examined in detail. Two important insights that can be gained from LCA techniques are

1. It is necessary to define a consistent system boundary around a process, so that most wastes associated with inputs (i.e., emissions from all preceding processes reaching right back to the original raw materials extraction) are included when the environmental impact of the process is assessed.
2. It is often more useful to concentrate on the environmental impact of the process emissions rather than the actual emissions, themselves. If a limited number of impacts can be assumed to be important (most LCA studies quantify 5 to 10 environmental impacts), then the inventory of emissions (which may comprise several hundred chemical species) can be reduced in dimension

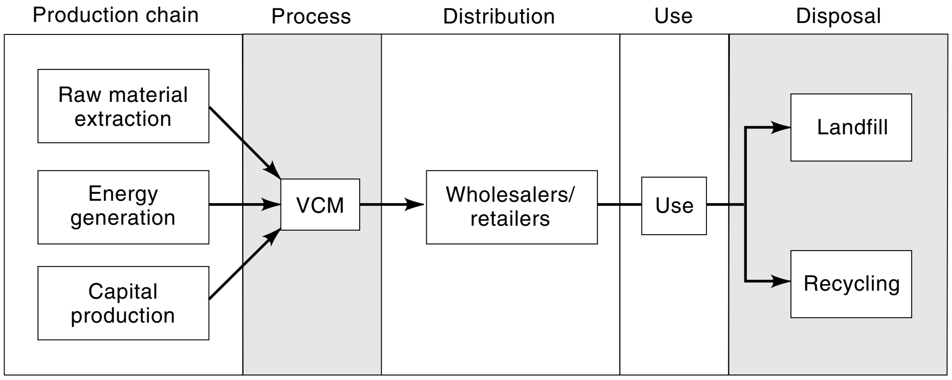


**Figure 1.** Boundary studied in criteria for VCM ecolabels.

> to an impact vector which comprises 5 to 10 elements. This greatly facilitates comparison of discharges which are ostensibly different in nature. Thus, instead of attempting to compare discharges of different chemicals, it is possible to transform the emissions inventory into a "common currency" comprising a limited number of environmental impacts and compare processes on this more manageable basis.

A design methodology for the assessment and minimization of the environmental impact of process systems is presented in this article. The proposed methodology relies on principles of Life Cycle and Risk Assessment that are embedded within a formal process optimization framework. Such an integrated environmental framework extends existing waste minimization design techniques by providing a considerably more complete description of the environmental impact of the process. It has implications to process synthesis by including environmental objectives together with economics at the design stage so as to determine cost efficient solutions to waste minimization projects. Furthermore, it adds to conventional life cycle and risk analysis tools by employing process modelling and optimization techniques to yield the optimal design/operating conditions and efficiently select the best materials to be used in order to achieve minimum environmental impact.

## MINIMUM ENVIRONMENTAL IMPACT METHODOLOGY

In order to systematically estimate and minimize the full range of adverse effects of processing systems on the environment, the following step-wise procedure is proposed.

### Definition of System Boundary

The boundary of the process of interest needs to be defined. The conventional system boundary helps to identify all waste output to the environment such as gaseous emissions, wastewater streams, leakages, etc. However, wastes associated with *inputs* to the process, such as raw materials and energy consumption, are not taken into account. For this purpose, the boundary of the process can be expanded to include all processes related to raw materials extraction, energy generation, and capital manufacture. Including all sources of pollution from natural sources to the gate of the process (cradle-to-gate analysis) provides the designer a global view of the process interactions with the environment. It should be noted that the methodology is flexible with respect to the choice of system boundary (conventional or global), as this depends as well on the aims of the specific case to be tackled, the target audience, and the data availability.

### Emissions Inventory

Within the system boundary, the emissions inventory is defined as the vector of all routine and nonroutine gaseous, liquid, and solid wastes disposed to the environment from all processes in the network. Intentional waste release is associated with discharges from planned operation of the process (for example, gaseous purge and wastewater streams), whereas unintended wastes mainly arise from accidental releases, emissions from process deviations (like start up, shutdown, changes in plant parameters, etc.), and fugitive emissions that are generally tolerated in industry. It is often the case that the resulting waste vector is highly dimensional; this prohibits the efficient analysis and interpretation of the environmental behavior of the process. Furthermore, the emissions inventory relies only on the mass of pollutant discharged and shows no indication of the form and extent of the actual damage caused to the environment.

**Table 1. Transformation of Emissions Inventory to Environmental Impact**

| Initial Vector | Condensed Vector |
|---|---|
| Energy Contents of Feed-stocks and By products | • Primary Energy |
| Processing Energy | |
| Transport Energy | |
| $C_1$s, $C_2$s | |
| $C_3$s | • Indirect Global Warming |
| $C_4$s | • Photochemical Oxidation |
| Others Volatile Organic Compounds | |
| $CO_2$, $CH_4$ | |
| CFCs, $N_2O$ | • Global Warming (Direct) |
| HCFCs, $CCl_4$, $CH_3CCl_3$ | |
| $SO_2$ | • Acid Rain |
| $NH_3$, CO | |
| $NO_x$ | • Toxic Air Pollutants |
| HCl, $SO_2$ | |
| Acids | |
| Heavy Metals | |
| Dissolved, Suspended Solids | • Toxic Water Pollutants |
| BOD | |
| Solid Wastes | • Solid Wastes |

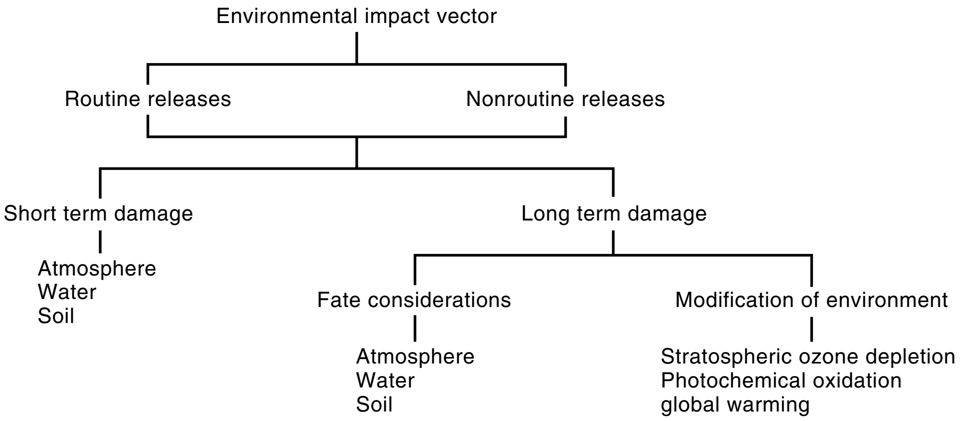


**Figure 2.** Environmental impact assessment options.

### Environmental Assessment of Routine Releases

In order to reduce the dimensionality of the problem and provide aggregate, yet accurate, information on the environmental burden associated with any industrial process, an environmental impact assessment step is included in the methodology. The essence of the environmental damage quantification is to transform the emissions inventory into an impact vector of low dimensionality. For this purpose, all routine releases are grouped together with respect to the form of burden caused. For example, as illustrated in Table 1, the initial waste vector is transformed to a condensed environmental impact vector that consists of metrics to measure pollution related to energy, global warming, air pollution, water pollution, etc.

While the metrics used to assess different aspects of pollution are analysed in subsequent chapters, the environmental impact assessment tool developed in this work is qualitatively presented in Fig. 2. The environmental damage caused by releases due to expected or unexpected operation can be broadly classified as follows.

**Short Term Environmental Effects.** Short term environmental assessment is the measurement of environmental damage at the point source of the release. The environmental burdens, in this case, depend on the legislation limits imposed (for example, threshold value, maximum acceptable concentration for discharge) and the mass of pollutant discharged. The point source impact can be distinguished into (1) atmospheric, representing qualitatively the amount of air necessary to dilute the pollutants down to the desirable concentration, (2) aquatic, referring to the equivalent amount of water volume (or mass) to meet the required limits, and (3) solid, associated with the total mass of solids disposed.

**Long Term Environmental Effects.** The long term environmental impact assessment mainly involves pollution that arises from post-release pollutant behavior and can be distinguished into two categories based on environmental or human-health concerns.

1. *Modification of the Environment.* The metrics used in this case deal with global atmospheric change problems of major public concern, such as greenhouse effect enhancement leading to global climate change and stratospheric ozone depletion. All the metrics used in this case represent relative environmental damage with respect to pollutants like carbon dioxide (global warming), ethylene (photochemical oxidation), and CFC11 (stratospheric ozone depletion).
2. *Fate Considerations.* Short term environmental impact assessment relies on the assumption that various pollutants contribute linearly to the overall environmental impact. This can be unrealistic in many cases since the actual partitioning and the reactions of each pollutant in the environment are ignored. To predict the post release behavior of pollutants, the multimedia approach developed by (24) is employed. The globe is assumed to comprise three primary media: air, water, and soil, in equilibrium. This form of environmental impact assessment is based on steady state behavior and continuous release scenarios. Furthermore, uniform pollutant distribution and first order exponential decay in each medium is assumed for all pollutants. The ultimate environmental impact is based on maximum acceptable concentration and reflects the actual damage caused in the environment based on the distribution of the pollutant in the various compartments.

### Assessment of Nonroutine Releases

The environmental impact assessment technique defined above can be extended to quantify not only routine process releases like purge, wastewater streams, etc., but also potential environmental hazards related to unexpected plant operation. As shown in the hypothetical risk frequency graph presented in Fig. 3, the nonroutine releases have significant

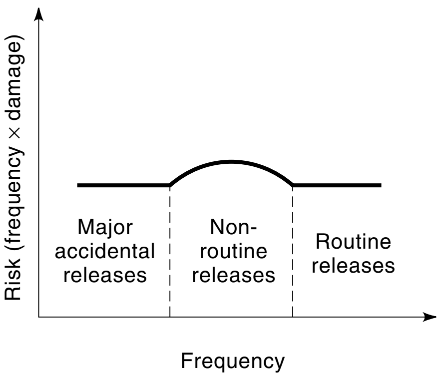


**Figure 3.** Risk frequency graph.

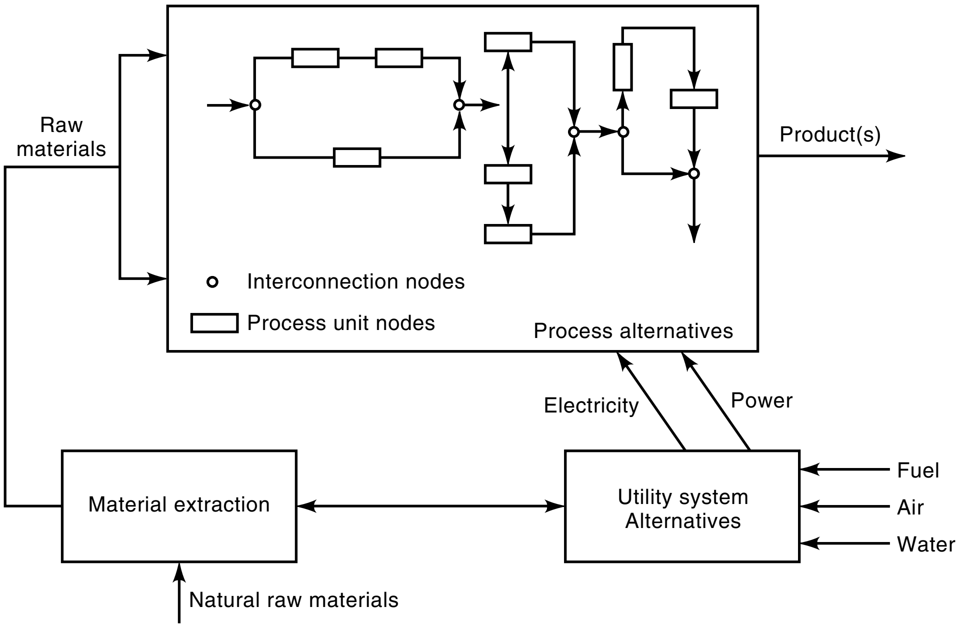


**Figure 4.** A general process system superstructure.

influence on the environmental damage related to a process system. Unlike extreme cases of major accidents that occur at very low frequencies but with serious consequences and routine releases that are highly frequent but cause minor environmental damage, nonroutine releases are placed within this frequency range posing often moderate adverse effects and, therefore, resulting in considerable risk levels. For this purpose, in addition to conventional environmental impact assessment, a quantitative risk analysis step is developed based on formal reliability assessment techniques, accounting for release scenarios for various types of nonroutine pollution related to internal events (such as releases due to equipment failure) or external events (such as fugitive emissions due to small leaks or spills from pumps or flanges) that are generally tolerated in industry. This information is then used to quantify the environmental impact vector of the fully operable state and the vector of nonroutine release environmental impact, defined as the weighted sum of deviations of all degraded operable states from the standard release scenario.

### Synthesis of Environmentally Benign Processes

The last step, which constitutes the heart of the methodology, is the incorporation of the environmental impact criteria presented in the previous section into an overall process synthesis and optimization strategy. The process synthesis problem then will conceptually involve determining the best design and plant operation featuring minimum environmental impact at minimum annualized cost. Different process technological and material alternatives are explicitly considered in a general process system superstructure, as shown in Fig. 4. For example, for the reaction section, alternative reaction routes possibly involving different raw materials, different types of reactors, and reactor network configurations can be included. For the separation section of the process, different separation systems, such as distillation, extractive distillation, adsorption, and hybrid separation systems, including reactive separation, can also be explicitly considered. Alternatives for material extraction (for raw materials, solvents, catalysts, and mass separating agents) and utilities (fuel, air, water, etc.) are included in order to ensure a global environmental impact assessment strategy.

Such a general synthesis strategy will then lead to a conceptual mathematical formulation as follows:

[P] min Annual Cost
(or max NPV)
and

min{Environmental Impact Criteria}
- routine releases
  - function of structural design and operating variations
- nonroutine releases
  - additional function of reliability models and stochastic events

(A)

s.t.

Superstructure global process model and design specifications
- Material and energy balances
- Physicochemical property equations
- Operational requirements (scheduling)
- Equipment design and specification constraints
- Logical conditions

(B)

Unlike conventional process, synthesis mathematical formulations based on a mixed integer optimization representation, problem [**P**] has three additional features:

- It involves, as explicit objectives, the minimization of environmental impact criteria in (A); that is, it is a multiobjective optimization problem

- Unlike conventional Life-Cycle Analysis tools, these environmental impact criteria have been modelled as explicit parametric expressions of structural design and operating (including reliability) process variables; that is, they are functions of the process decisions
- It involves global considerations in a plant-wide context in (B)

These additional three features conceptually differentiate problem [**P**] to conventional process synthesis formulations; in this respect, the above problem can be viewed as a conceptual process synthesis problem formulation for obtaining environmentally benign processes on a plant-wide basis.

The solution of the above problem clearly poses a number of difficulties and challenges. While this article does not aim to address all numerical issues involved in the efficient solution of problem [**P**], it is shown in the next sections, how formal multiobjective optimization techniques (see for example, (25) can be applied to certain classes of [**P**] to obtain the Pareto space of (parametric) optimal solutions with respect to cost and the various components of environmental impact. Material design issues are also captured in [**P**], as discussed next.

## LIFE CYCLE OPTIMIZATION IN CONTINUOUS PROCESSES

The production system of dichloroethane from hydrochloric acid, ethylene, and oxygen by oxychlorination is studied here as a means of revealing waste minimization opportunities and demonstrating the need for a consistent framework to investigate the environmental impact of continuous processes.

Dichloroethane (DCE) is an intermediate for the production of vinyl chloride monomer. Hydrogen chloride, ethylene, and oxygen (either in air or as a pure gas) react in a fixed reactor as presented in Fig. 5, which operates at constant pressure (5 atm) and temperature (220 °C), in the presence of a small amount of catalyst (copper chloride) (26). The reaction selectivity is high, and DCE purity exceeds 98%, with negligible amounts of chloral and ethyl chloride. A small portion of the ethylene feed is oxidized to carbon monoxide and carbon dioxide. The products and unreacted raw materials exit the reactor and are separated using a three phase flash drum. The bottom exit stream mainly consists of DCE, $H_2O$, and traces of dissolved gases which are removed from the DCE using a distillation column. The side aqueous phase consists of water which is contaminated with DCE and traces of gases. The unreacted gases such as $C_2H_4$, $O_2$, $N_2$ (in case of air feed), and HCl are separated and exit as the vapor phase. The aqueous exit stream from the flash drum is fed to a suitable separation stage (possible alternatives are a steam stripper or a distillation column) for removal of the residual (undesirable) DCE. The vapor stream mainly consists of unreacted gases and is fed to a burner. Thus, the main emissions from this simplified process flowsheet are the waste gases, which are fed to a burner operating at sufficiently high temperature to ensure effectively 100% combustion, and the DCE contaminated wastewater stream which is partially cleaned up in the stripping or distillation column.

A typical waste minimization approach could be applied to obtain the optimal operating conditions of the process that minimize its annual cost, not entailing excessive waste generation. The superstructure of the continuous process to include alternative raw materials (such as air or pure oxygen) and separation techniques (steam stripping, distillation), in the most general case can be modelled as a mixed integer nonlinear (MINLP) optimization problem of the following form (27):

$$Z = \min\{c^T \cdot y + f(x)\} \tag{1}$$

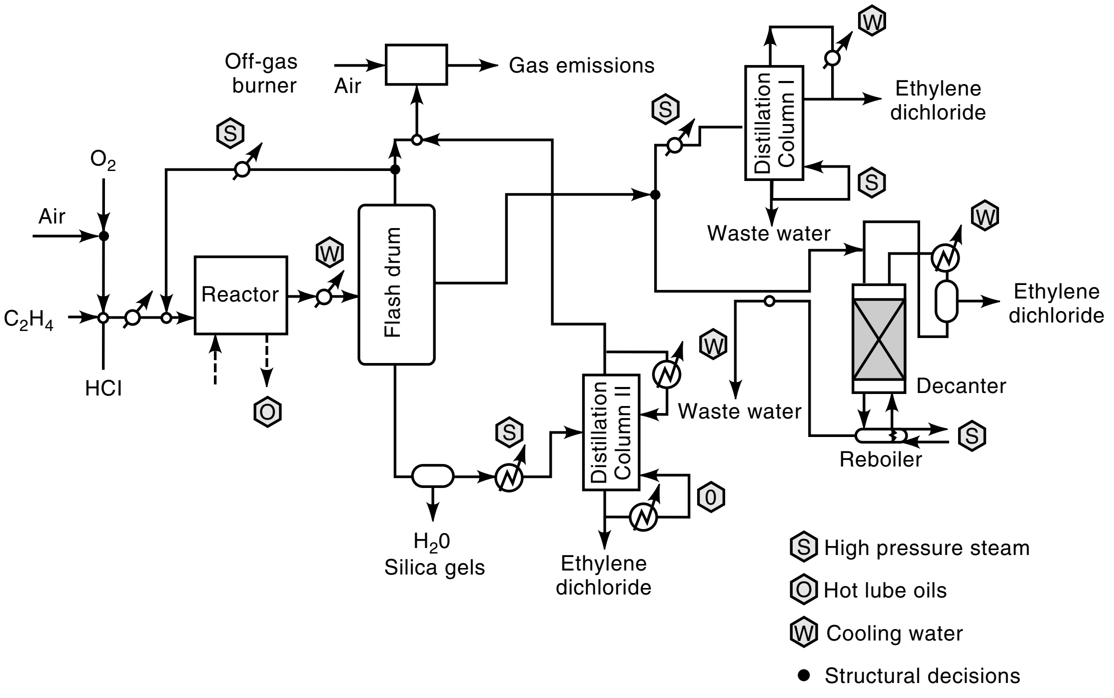


**Figure 5.** The dichloroethane production process.

s.t.

$$h(x) = 0$$

$$g(x) \leq 0$$

$$A \cdot x = a$$

$$B \cdot y + C \cdot x \leq d$$

$$x \in X = \{x | x \in R^n, x^L \leq x \leq x^U\}$$

$$y \in Y = \{y | y \in 0, 1^m\}$$

$$p(x) \leq p^U$$

The continuous variables **x** represent flows, operating conditions, and design variables. The binary variables **y** denote the potential existence of process unit blocks and streams. These variables typically appear linearly as they are included in the objective function to represent fixed charges in the purchase of process equipment (in the term $c^T \cdot y$) and in the constraints to enforce logical conditions ($B \cdot y + C \cdot x \leq d$). The term $f(x)$ is often a linear term involving purchase costs for process equipment (cost coefficients, multiplying equipment capacities, or sizes), raw material purchase costs, product/by-product sales revenues, and utility costs. The sizing equations correspond to $h(x) = 0$, and the inequality constraints $g(x) \leq 0$ include design specifications which are typically linear inequalities. The linear equations include mass balances and relations between the states of process streams. Pollution metrics can be expressed in terms of flowrate or stream concentration, and constraints are imposed for pollution prevention ($p^U$ denote the desired upper bounds). The best structure and the corresponding optimal values of the operating variables of problem (1) are presented in Table 2.

If one concentrates on the waste water stream exiting from the last column or the steam stripper, it can be noted that minimization of annual cost results in relatively large DCE mole fractions in the exit stream. This is expected as applying stricter limits on the DCE mole fraction results in an increase of the column (stripper) size and steam consumption. By solving parametrically problem (1) for varying mole fractions, one realizes that an increased cost penalty has to be paid for waste minimization (Fig. 6). Steam stripping and oxygen feed appear to be cheaper alternatives, despite the fact that oxygen is a more expensive raw material than air, since air flowrates significantly increase equipment sizing.

**Table 2. Optimal Operation of DCE Process for Minimum Total Annual Cost**

| Raw Material | Oxygen |
|---|---|
| Separation Alternative | Steam Stripping |
| Conversion of Hydrogen Chloride ($0.93 \leq x_{\mathrm{HCl}} \leq 0.97$) | 0.93 |
| Flash Drum Temperature ($T_F \geq 313$ K) | 313 |
| Flash Drum Pressure ($202 \leq P_F \leq 510$ kPa) | 250 |
| Stripping Column Pressure ($101.3 \leq P_{Str} \leq 202$ kPa) | 101.3 |
| Distillation Column II Pressure ($P_{\mathrm{DII}} \leq 202$ kPa) | 180 |
| DCE Mole Fraction in Waste Water Stream ($x_{\mathrm{DCE}} \leq 10^{-4}$)) | $1 \times 10^{-4}$ |
| TAC (rcu/y) | $1.74 \times 10^6$ |

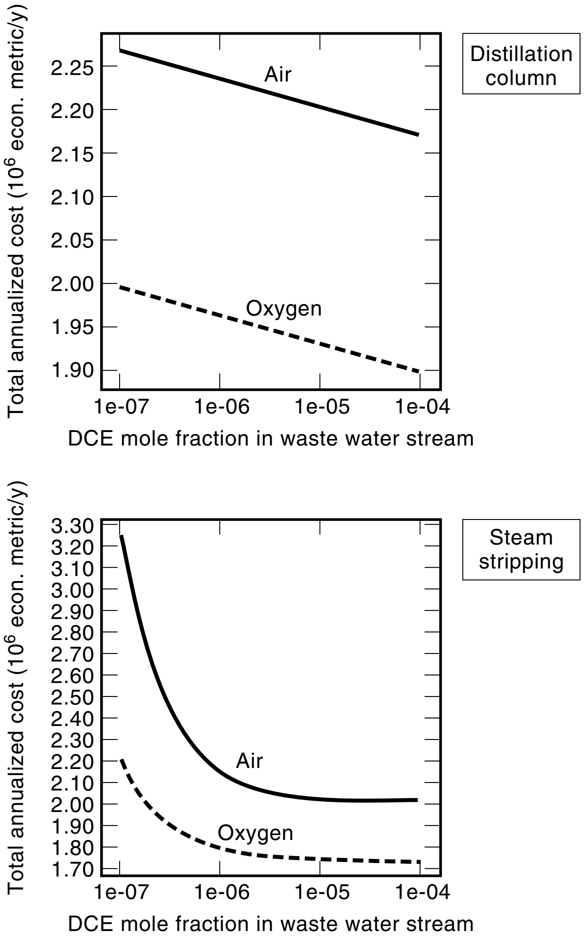


**Figure 6.** Effect of the DCE degree of abatement on the annual cost of the process.

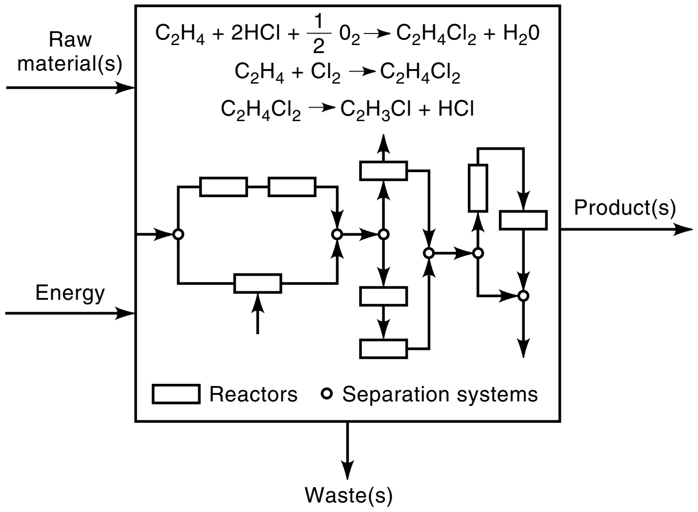
However, such an analysis takes a myopic local view of environmentally related problems. For example, although DCE exits in the waste water stream, due to its high volatility, much of it becomes airborne, so ideally, a metric should be used to combine the DCE discharge with the gaseous discharge from the tail gas burner and facilitate the minimization of the overall pollution at the same time, without solving independent optimization problems for each type of waste. An obvious question that arises here is, then, "Can (a) common metric(s) be defined to enable the minimization of ostensibly different emissions at the same time?". Another issue is the following: dichloroethane, for example, also affects the global warming phenomenon, and therefore, this effect needs to be taken into account in quantifying the overall impact of the process. A second question is then: "Apart from the common pollution effects, such as air emissions, water pollution, and solid discharge, is it possible to explore long term environmental effects (such as global warming, ozone depletion etc.) and obtain a more complete picture about the interactions of the process with the environment?".

In minimizing the cost subject to waste constraints in the example above, it was implicitly assumed that all the pollution effects were due to the DCE waste and the off-gases. However, in order to purify the wastewater stream, a large amount of steam is consumed that generates an additional waste input to the process. In addition, the raw material generation and the capital manufacture create waste inputs that need to be taken into account.

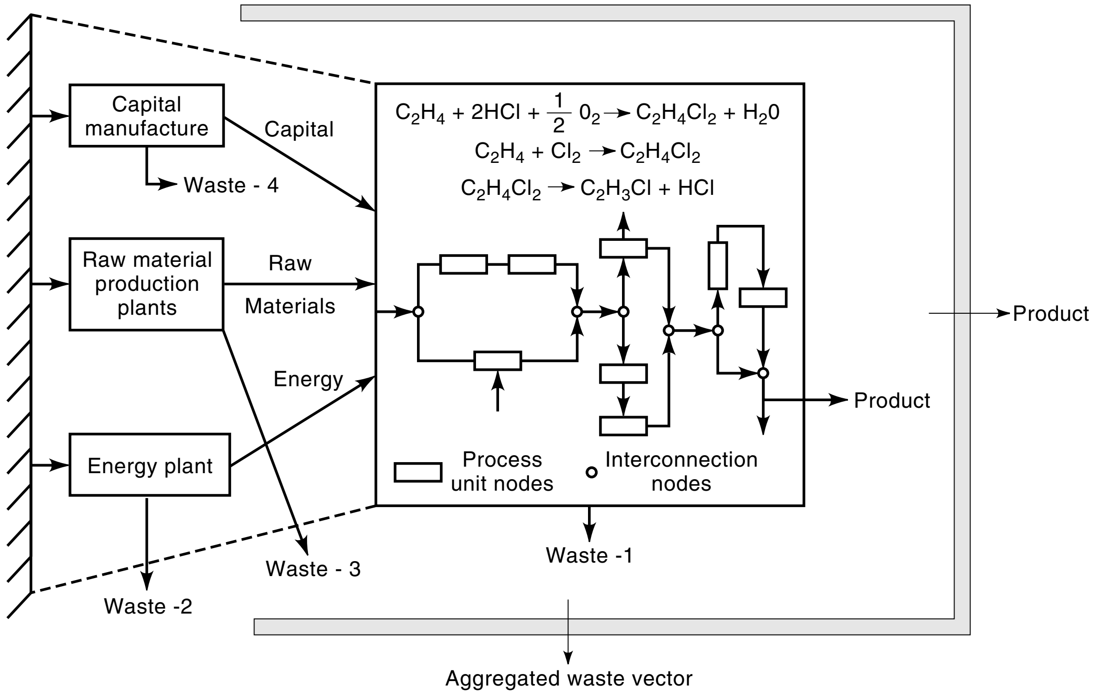
These important dimensions of the environmental impact minimization and pollution prevention problem in continuous processes can be effectively captured by the proposed methodology for environmental impact minimization.

### Definition of Process System Boundary

This step involves expansion of the conventional process system boundary to include all processes associated with raw materials extraction and energy generation. As shown in Fig. 7, this requires backtracking from the conventional process system all the way to the natural state of pure raw materials which are available at no environmental penalty. Different technological routes for the production of the same set of raw materials (leading to desired product formation) are included in this expanded boundary. The advantage of defining such an expanded global process system boundary is that input (to the conventional process) wastes together with their routes can also be accounted for together with output emissions forming an aggregated waste vector (see Fig. 7). Note that although this definition is consistent with the one used in Life Cycle Analysis (22), it does not include the routes and stages of the product after leaving the process since the main focus of this work is on optimizing the damage related to a chemical manufacturing route.



(**a**) Conventional process system boundary



(**b**) Expanded "global" process system boundary

**Figure 7.** Definition of global process system boundary.

Different waste treatment systems associated with process waste effluents can be explicitly considered, although conceptually achieving minimum environmental impact without any waste treatment provides a target treatment value for any possible waste treatment system.

### Environmental Impact Assessment

Having defined a global process system boundary, an assessment of the environmental impact of the various wastes (the aggregate waste vector in Fig. 8) flowing out of the system is performed in step 2. This involves (1) defining an emissions inventory comprising all wastes generated in any stage of the processing network within the global process systems boundary, and (2) grouping these wastes together according to their impact on the environment—this is termed environmental impact assessment.

Environmental impact is commonly assessed by defining appropriate environmental indices, which measure air pollution, water pollution, solid wastes, global warming, photochemical oxidation, and stratospheric ozone depletion. There is considerable debate surrounding impact assessment (see, for example, Ref. 28); yet currently, there is no sound scientific way of arriving at sensible quantitative metrics for overall environmental impact—a subject of active research work.

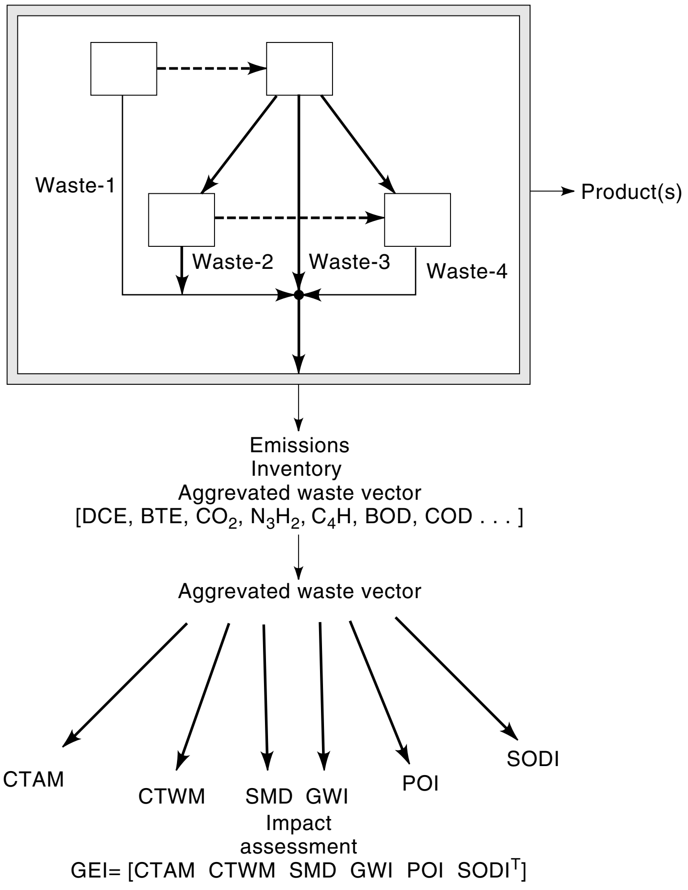


**Figure 8.** Environmental impact assessment.

Air pollution is measured by defining a critical air mass (CTAM) as kg air/h,

$$\mathrm{CTAM} = \frac{\text{Mass of air emissions (kg pollutant/h)}}{\text{Standard limit value (kg pollutant/kg air)}}$$

water pollution by a critical water mass (CTWM) as kg water/h,

$$\mathrm{CTWM} = \frac{\text{Mass of Water Pollutant (kg pollutant/h)}}{\text{Standard Limit Value (kg pollutant/kg water)}}$$

and solid wastes by a solid mass disposal (SMD) as kg solids/h.

In all the above metrics, the mass of pollutant discharged is assumed to be measured at the point source of the release. Long term interactions like global warming can be depicted by metrics like global warming impact (GWI) as kg $CO_2$/h:

$$\mathrm{GWI} = \text{Mass of Pollutant (kg/h)} \times \mathrm{GWP}(\text{kg } CO_2\text{/kg pollutant})$$

where GWP is the global warming potential of each pollutant. Similarly to GWI, photochemical oxidation is defined by photochemical oxidation impact (POI) as kg ethylene/h:

$$\mathrm{POI} = \text{Mass of Pollutant (kg/h)} \times \mathrm{POCP}(\text{kg } C_2H_4\text{/kg pollutant})$$

where POCP is the photochemical oxidation potential as in UK Ecolabelling Board Report (21) and stratospheric ozone depletion by stratospheric ozone depletion impact (SODI) as kg CFC11/h:

$$\begin{aligned}\mathrm{SODI} &= \text{Mass of Pollutant (kg/h)} \\ &\quad \times \text{SODP (kg CFC11/kg pollutant)}\end{aligned}$$

where SODP is the stratospheric ozone depletion potential (SODP), as in UK Stratospheric Ozone Review Group Report (29). Note that the direct global warming potential is defined as (30):

$$GWP_w = \frac{\int_o^\infty a_w(t) c_w(t)\, dt}{\int_o^\infty a_c(t) c_c(t)\, dt}$$

where $a_w(t)$ is the instantaneous radiative forcing due to a unit increase in the concentration of waste gas $w$, and $c_w(t)$ is the fraction of the gas $w$, remaining at time $t$. The corresponding values of $CO_2$ are in the denominator. Radiative forcing is expressed as the initial change in earth's radiation budget due to changes in the greenhouse gas concentrations ($\mathrm{Wm^{-2} p.p.m.^{-1}}$).

As a result, for each pollutant $w$ (for example, DCE), a vector $\boldsymbol{EI_w}$ can be obtained denoting its corresponding environmental impact; that is,

$$EI_w = [\mathrm{CTAM\ CTWM\ SMD\ GWI\ POI\ SODI}]_w^T$$

By summing up all pollutants, a global environmental impact vector can be obtained indicating the environmental impact of the entire processing network, as shown in Fig. 8:

$$\mathrm{GEI} = \sum_{w=1}^{W} EI_w = [\mathrm{CTAM\ CTWM\ SMD\ GWI\ POI\ SODI}]_{\mathrm{process}}^T$$

There are two advantages of using a global environmental impact vector (GEI):

- The vector of waste emissions typically comprising a large number of wastes can effectively be transformed into an aggregated vector of low dimensionality (in this case, of six)
- The information provided is directly linked to impact on the environment rather than, for instance, to mass flowrates of waste materials.

Note that this systematic aggregation of wastes relative to their environmental impact obviously can be used for both conventional and expanded (global) process system boundaries. Furthermore, the use of environmental impact vectors does not exclude the possibility of employing them in conjunction with other environmental "indicators" (for example, BOD or a specific pollutant mass discharge) if environmental legislation enforces such limits.

### Incorporation of Environmental Impact Criteria in Process Synthesis and Design Optimization

The third step of MEIM involves the direct incorporation of environmental impact criteria in a conceptual process synthesis formulation, discussed earlier (problem [**P**]). Using the notation of problem (1), problem [**P**] can then be revisited as follows:

$$\min_{x,y} [c^T y + f(x),\ GEI] \tag{2}$$

s.t.

$$h(x) = 0$$
$$g(x) \le 0$$
$$A \cdot x = a$$
$$B \cdot y + C \cdot x \le d$$
$$x \in X, y \in Y$$
$$GEI(x, y) = [\text{CTAM CTWM SMD GWI POI SODI}]^T_{\text{process}}$$
$$p(x) \le p^u$$

Equation (2) is a multiobjective mixed-integer nonlinear programming problem. One way to solve Eq. (2) is to reformulate it as the following parametric MINLP problem ($\epsilon$-constraint method).

$$\min_{x,y} c^T y + f(x) \tag{3}$$

s.t.

$$h(x) = 0$$
$$g(x) \le 0$$
$$A \cdot x = a$$
$$B \cdot y + C \cdot x \le d$$
$$x \in X,\ y \in Y$$
$$GEI(x, y) \le \epsilon$$
$$p(x) \le p^u$$

where $\epsilon$ is a parameter vector.

Acevedo and Pistikopoulos (30) have recently developed new algorithms for the rigorous solution of problems such as (3). The solution of problem (3) for fixed structural decisions (fixed **y** vector) yields the Pareto curve of noninferior solutions, as shown in Fig. 9(a). If structural alternatives are also included, the solution of (3) may be discontinuous, as shown in Fig. 9(b), where different segments correspond to different optimal structural arrangements.

### Remarks on Benefits of MEIM

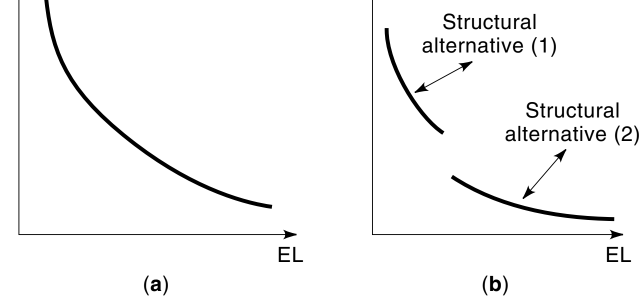
The methodology for environmental impact minimization, as described above, in principle enables one to:

- Obtain compromise solutions in a systematic way by transforming the traditional process design style optimization problem, typically involving a cost/profit objective function, to be a multiobjective optimization problem [see Figs. 10(a,b)],
- Show that zero emissions may not be the best environmental policy, but rather seek for optimal degree of abatement [see Fig. 11(a)], and
- Identify pollution prevention strategies which also result in cost savings [see Fig. 11(b)]

**Example 1.** The proposed methodology is applied to the DCE example described above.

### Definition of System Boundary

Figure 12 shows a block representation of the DCE production process and the processes associated with the generation of all raw materials required in the DCE manufacture. A conventional waste minimization approach would focus on arriving at the minimum cost subject to emissions constraints on discharge of DCE from the production process; in our simplified flowsheet (Fig. 5), this corresponds to meeting a constraint on emissions of DCE from the steam stripper or the distillation column. Generally, wastes associated with inputs to the process such as raw materials and energy are ignored. In MEIM, environmental impacts associated with all process inputs are included by associating an impact vector with each input, which contains information on the aggregated environmental impact of the input, incorporating all processing stages back to the extraction of raw materials. Raw materials such as air, rock salt, and coal are assumed to be available at



(a) (b)

**Figure 9.** Pareto curve of noninferior solutions between cost and environment: (a) Pareto curve for fixed structure. (b) Impact of structural changes on Pareto curve.

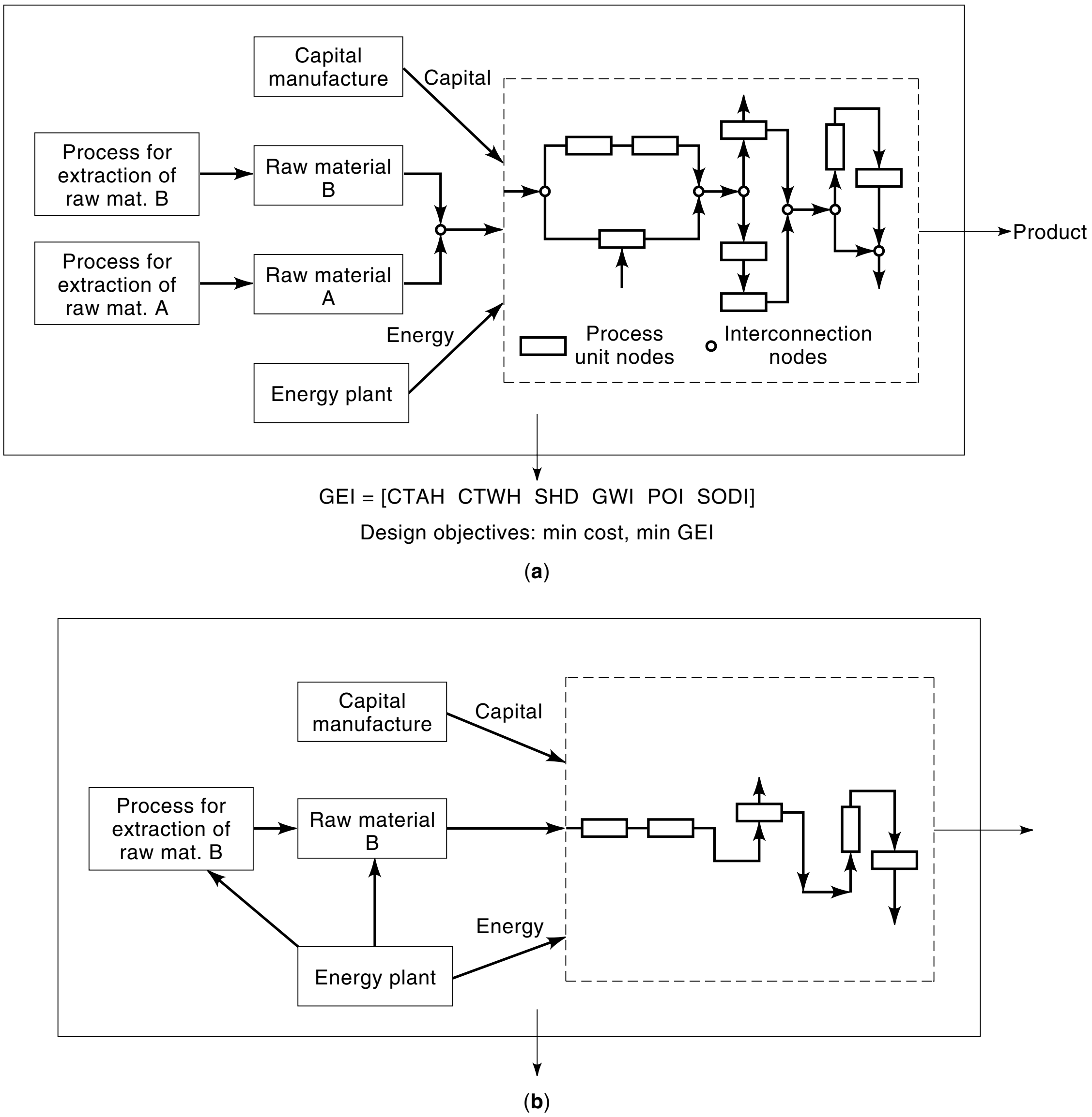


**Figure 10.** Incorporation of environmental impact criteria in process synthesis and design optimization: (a) Multiobjective optimization framework, (b) “best” manufacturing route for minimum environmental impact (from possible technological alternatives).

no environmental penalty. This approach requires analysis of environmental impacts associated with the production of energy, hydrochloric acid, ethylene, and in the case of pure oxygen feed, air separation. Each of these inputs has an associated environmental impact vector which can be obtained through an environmental impact assessment, as described below.

### Environmental Impact Assessment

**Emissions Inventory.** Once a clear system boundary has been drawn, it is possible to determine an emissions inventory for the system. Raw materials flow inwards across the system boundary, and products and emissions flow out. For DCE production, the emissions comprise DCE exiting in the wastewater stream, water exiting in the wastewater stream, and carbon dioxide exiting in the tail gas from the burner. Note that oxygen and nitrogen, which flow across the system boundary into the process and flow out again, are not considered as emissions, since they enter from the natural resource state and then exit to the natural resource state. In a similar fashion, inventories can be prepared for the processes in which production of raw materials (HCl, ethylene) and energy take place.

Each raw material is extracted from its natural state (Fig. 12). In particular, ethylene is produced from naphtha (32), which is a major product of the petroleum mining and processing plant (33). Hydrogen chloride is generated directly from hydrogen and chloride using the anhydrous HCl process (34). The chlorine feed is assumed to be pure and is produced from electrolytic chlorine cells (33). All hydrogen feed to the HCl manufacture plant is produced from the electrolysis process (as a by-product). Rock salt is needed as feed to generate chlorine and hydrogen (35); therefore, wastes associated with

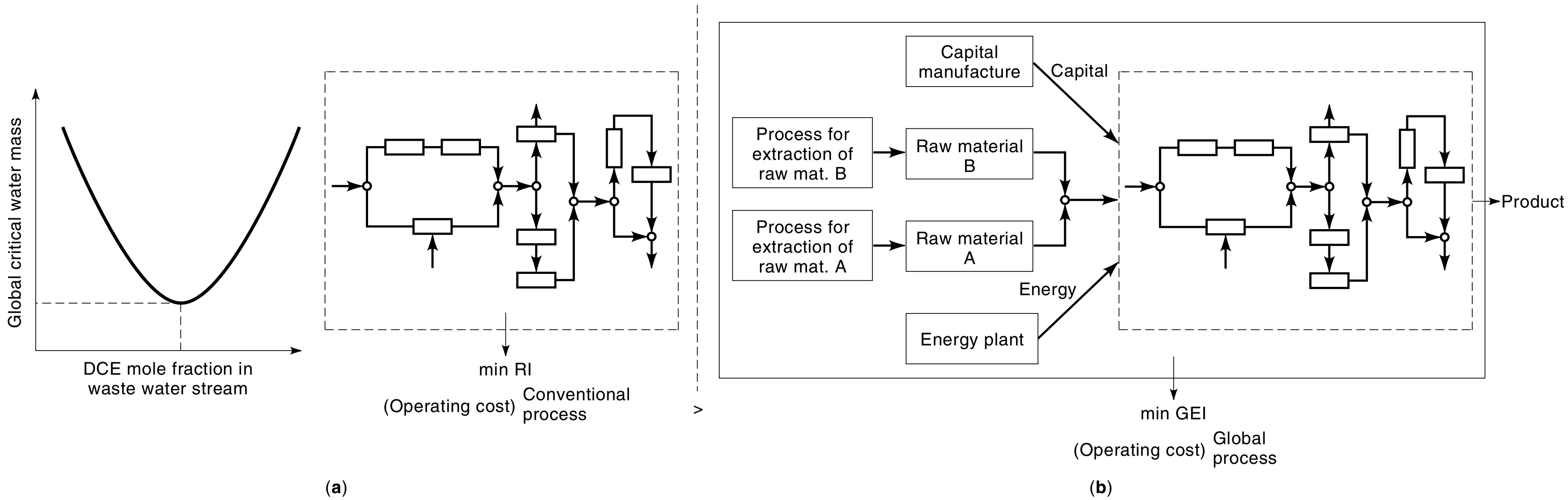


**Figure 11.** Benefits of methodology for environmental impact minimization: (a) Optimal degree of abatement, (b) MEIM may result in operating cost savings!

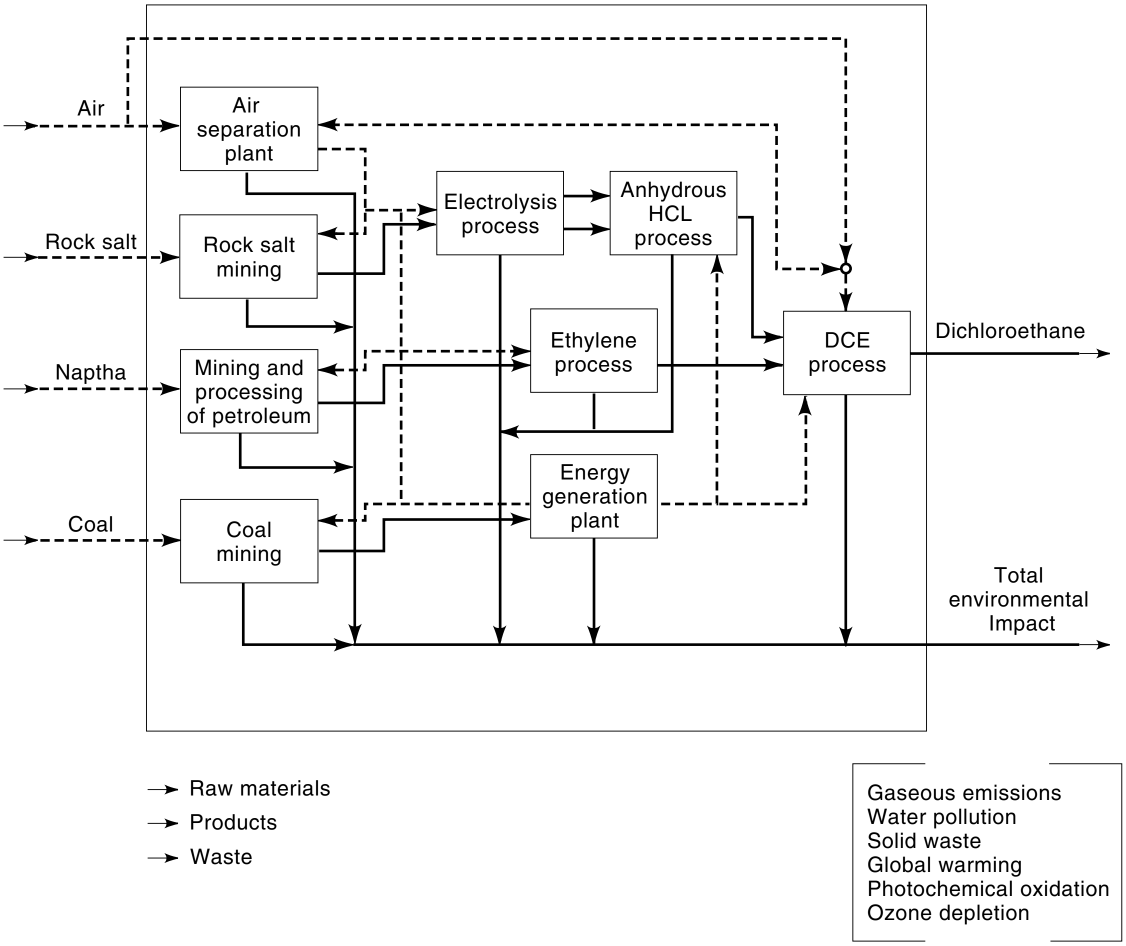


**Figure 12.** The global dichloroethane production system.

rock salt mining must be considered. The net energy demand for the process of interest and all associated processes is satisfied by a power generation plant using coal as raw material input (33) [there sometimes arise cases in which there is an energy credit if energy is generated in a process, such as in this case where energy is produced due to the highly exothermic oxychlorination reaction (34)]. Finally, for the case in which oxygen is fed into the oxychlorinator, an air separation plant has to be taken into account (36).

**Impact Assessment.** A key element in LCA is the transformation of an emissions inventory, which is simply a list of mass discharges of various chemical species into a series of environmental indices which reflect environmental impacts. Typical indices include measurements of the relative impacts of discharges on global warming [assigning carbon dioxide value of 1.0, methane, for instance, gets a relative rating of 30 (37)], stratospheric ozone depletion, and photochemical ozone creation potential. Such relative ratings can be determined through laboratory experiments and a knowledge of the physical processes involved in creating the pollution problem. The Critical Air Volume (Mass) represents the volume (mass) of air polluted by a given mass of pollutant discharged. Clearly, the critical volumes depend directly on the acceptable limit values. This is a problem if they are set arbitrarily; however, they can be set on a scientific and common basis; for instance, the US EPA uses dose-response analysis to set limit values so that all discharges result in approximately the same estimated increase in mortality rates. This issue is further complicated by the different half lives of emissions in the environment, and there is still considerable debate surrounding impact assessment. It would be useful if there was a sound way of combining the various indices to arrive at a single overall environmental impact index. Some authors (38) have suggested making what are essentially arbitrary combinations of impact indices to this end, but there seems little basis for their weight factors. For the purposes of the case study, we will simply employ two commonly used indices for analysis of the DCE manufacturing process: critical air volume based on point source releases and global warming potential.

We choose critical air volume because although DCE is discharged in a wastewater stream, it is a highly volatile compound and will partition heavily into air. DCE has a Henry's law constant of 529 atm/mole fraction. Given the total masses of air and water are $5.1 \times 10^{18}$ and $1 \times 10^{18}$ kg respectively, and since for sparingly soluble gases Henry's law constant $\mathscr{H}_g$ (atm/mole fraction) can be related to the dimensionless equilibrium constant $K^\infty$ as,

$$K^\infty = \left(\frac{y}{x}\right)_{x\to 0} = \frac{\mathscr{H}_g}{P}$$

it can be found that 99.9% of DCE on the earth would be present in the atmosphere, assuming perfect mixing.

To illustrate the calculations of critical air volume and global warming associated with a DCE discharge, consider a mass discharge of 1 kg of DCE in air. With a global warming index of 100 kg $CO_2$, and a limit value of 4 mg/$m^3$ air imposed by World Health Organization, WHO (39), the 1 kg discharge of DCE results in the following impact vector:

$$\begin{bmatrix} 2.5 \times 10^5 \text{ kg air} \\ 100 \text{ kg } CO_2 \end{bmatrix}$$

Such a calculation implicitly assumes a constant marginal impact for each pollutant; that is, 1 kg of DCE will have the same effect regardless of the existing extent of DCE pollution. While this may not be easily justified, there does not currently appear to be any better way of performing the calculation. In this case of constant marginal impact, the transformation of emissions inventories to impacts is essentially a matrix multiplication procedure. As an example, consider the following calculation for determining the impact of a discharge of 1 kg of DCE and 1 kg of methane [limit value = 15 mg/$m^3$ air (33); global warming index = 11 (37)]:

$$\begin{bmatrix} 2.5 \times 10^5 & 6.7 \times 10^4 \\ 100 & 11 \end{bmatrix} \cdot \begin{bmatrix} 1 \text{ kg DCE} \\ 1 \text{ kg } CH_4 \end{bmatrix} = \begin{bmatrix} 3.17 \times 10^5 \text{ kg air} \\ 111 \text{ kg } CO_2 \end{bmatrix}$$

In this case study, we are assuming a world in which the only environmental problems are air toxicity and global warming regardless of the dimension of the emissions inventory; thus, the dimensionality of the problem is considerably reduced. Moreover, this idea provides a technique for determining the additive impact of several processes. To see this, consider the hydrochloric acid production process and the DCE production process. The principle emission from the hydrochloric acid production process is a vent stream from the tails tower consisting mainly of hydrogen chloride, chlorine, and hydrogen, while the principle emission from the DCE production process is DCE. At first glance, it is not obvious how these should be combined to arrive at a combined impact, except by adding the masses discharged, which fails to take account of toxicity. However, using impact analysis, we simply calculate an impact vector for each process and add them, thus arriving at the total impact of both processes in terms of air toxicity and global warming. By working with the actual environmental impacts, rather than the discharges themselves, we are able to value widely varying processes in a common environmental impact currency.

**Incorporation of Environmental Impact Minimization Criteria in Process Optimization.** The critical air mass index (and global warming index) obviously depends on the process design and operating conditions; consequently, impact assessment also directly relates to process decisions. Therefore, the environmental impact vectors are expressed via input-output relationships across the processes within the global production system as functions of process decisions.

The environmental impact vector considered in the case of the DCE production process comprises the critical air mass, CTAM and the global warming potential, GWI (since no solid wastes are disposed, and the only gaseous waste of the process is the unreacted hydrogen chloride which has negligible global warming potential).

Table 3 summarizes the twenty case studies performed for the DCE production system. First, the conventional DCE process was considered with two different separation alternatives, distillation or steam stripping, and with two different raw materials, oxygen or air. Three independent criteria were used for the production of 1200 kg/h ethylene dichloride, the minimization of total annualized cost, the minimization of critical air mass (CTAM), and the minimization of global warming impact. The results concerning the annualized cost minimization have already been presented above.

For the conventional DCE production system, the results of the optimization study for the minimization of critical air mass, CTAM, and global warming, GWI, respectively (cases $c_I$, $d_I$, $f_I$ in Figs. 13, 14, and 15) verify what is intuitively expected; that is, environmental impact decreases as the degree of abatement increases—the case of air feed consistently gave higher pollution metrics for both separation alternatives. On the other hand, when the global production system was considered, the results (see cases $c_{II}$, $d_{II}$, $f_{II}$ in Figs. 13, 14, and 15) suggest that there is an optimal degree of abatement; that is, a threshold value of DCE mole fraction in waste water stream, above which the global environmental impact in fact increases. This is due to the underlying trade-off in waste generation between inputs to the system and outputs of the system. The existence of such a minimum threshold value clearly implies that from a global environmental point of view, the objective of minimizing "output" emissions of the system may in fact be suboptimal and illustrates the impossibility of achieving a zero environmental impact. As far as raw materials are concerned, the results of our analysis indicate that oxygen was consistently proven to be environmentally sounder on a global basis despite the cumulative impact generated from the air separation plant; the use of air increases substantially the impact of tail-gas burner emissions. For the case study considered here, steam stripping was found to be

**Table 3. DCE Production System: Case Studies Considered**

| Objective / System Boundary | Minimize COST | | Minimize CTAM | | Minimize GWI | |
|---|---|---|---|---|---|---|
| | Distillation | Steam Stripping | Distillation | Steam Stripping | Distillation | Steam Stripping |
| Conventional DCE | $a_I^{o,a}$ | $b_I^{o,a}$ | $c_I^{o,a}$ | $d_I^{o,a}$ | $e_I^{o,a}$ | $f_I^{o,a}$ |
| Global DCE | | | $c_{II}^{o,a}$ | $d_{II}^{o,a}$ | $e_{II}^{o,a}$ | $f_{II}^{o,a}$ |

o = oxygen
a = air feed

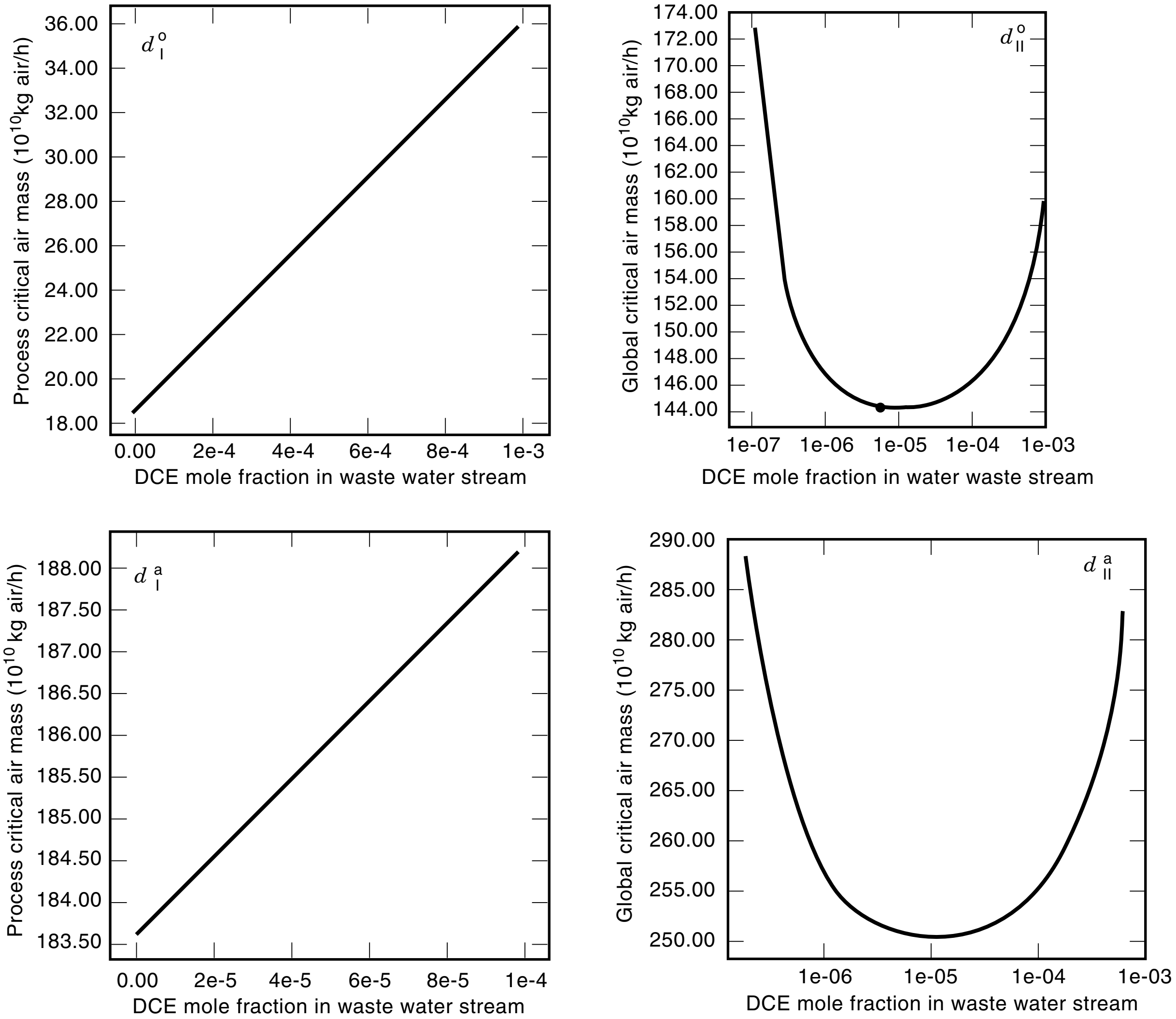


**Figure 13.** Effect of the degree of abatement on the optimal critical air mass impact of the DCE system (stripping case).

a cleaner design alternative; the increased steam consumption of the distillation column reboiler creates a dominant impact factor (see Fig. 15). Table 4 depicts the optimal operating conditions for cases $d^o_{II}$ and $f^o_{II}$ (both involving oxygen and steam stripping), which correspond to the process alternatives with the minimum global critical air mass (of $1.44 \times 10^{12}$ kg air/h) and minimum global warming impact of (1290 kg $CO_2$/h), respectively. The advantage of employing formal process optimization techniques for global environmental impact analysis is shown in Table 5. The optimal value of the process critical air mass impact for case $d^o_I$ (conventional process using oxygen-steam stripping) is $19 \times 10^{10}$ (see Fig. 13). Based on these operating conditions, by expanding the system's boundary (global DCE), a global critical air mass can be obtained at a value of $1.46 \times 10^{12}$, which is higher than the minimum global critical air mass impact value of $1.44 \times 10^{12}$. Therefore, for environmental impact analysis to be rigorous, process optimization has to be simultaneously carried out for the global production system. Finally, Fig. 16 summarizes the effect of increasing the environmental legislation limits of DCE on the global critical air mass impact. Stricter regulations decrease dichloroethane concentration in the wastestream; albeit, global environmental impact increases! Such analytical results may have profound implications to legislation as guidelines for setting acceptable environmental limits.

## LIFE CYCLE OPTIMIZATION IN BATCH/SEMICONTINUOUS PROCESSES

A key characteristic of batch plants is their inherent operational flexibility in utilizing available resources (equipment, utilities, production time). This feature introduces an extra complexity in the design of such plants since design considerations are interlinked with operational/scheduling aspects. This, in turn, implies that waste generation in batch plants depends on both design and scheduling decisions over a time horizon, related to product sequencing, task scheduling, the need for cleaning, as well as type and sizes of equipment. Another key issue for consistent environmental impact assessment is the need to translate waste generation over time to some measure of environmental damage as well as to account

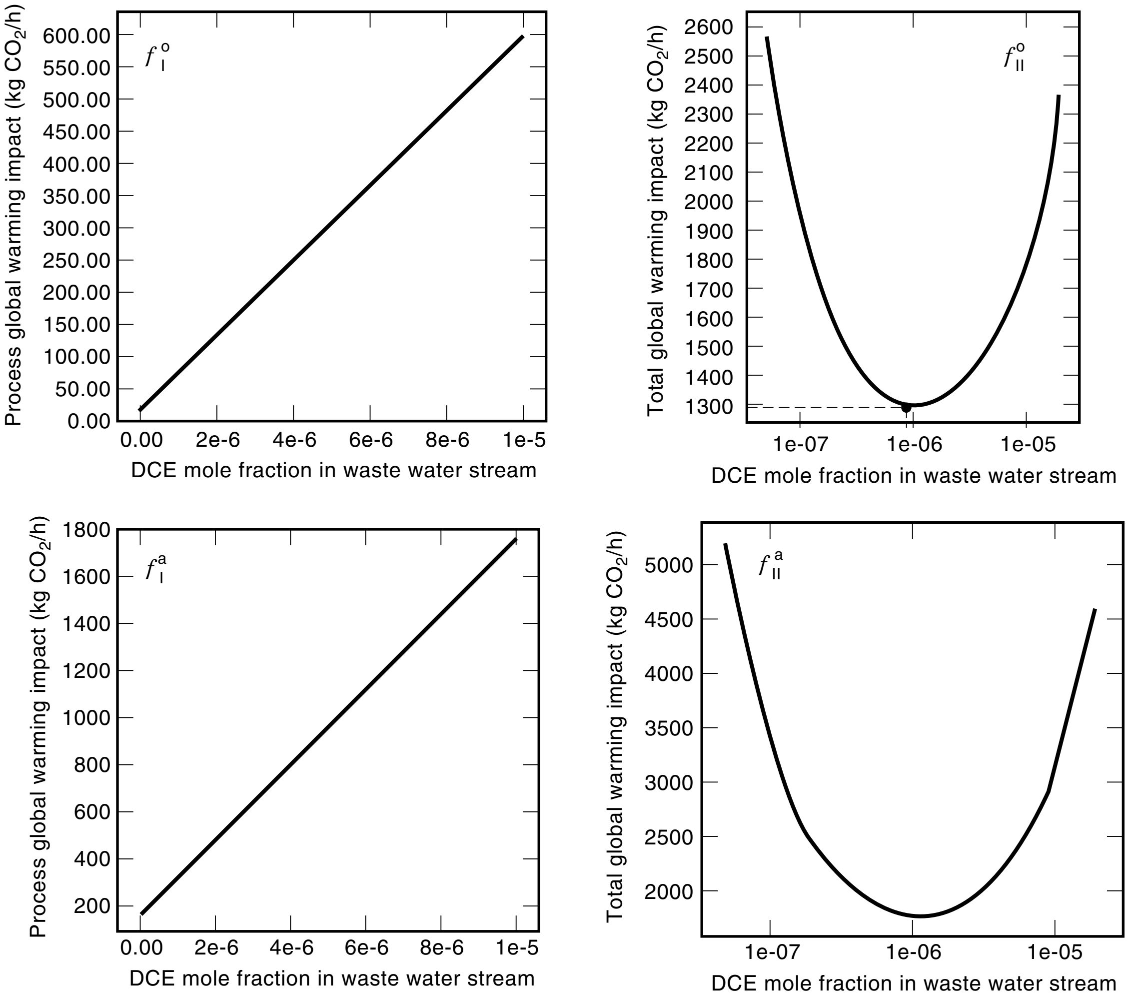


**Figure 14.** Effect of the degree of abatement on the optimal global warming impact of the DCE system (stripping case).

for input wastes (to the process) and their interactions with output waste generation.

Having defined a global system boundary for the batch plant, an assessment of the aggregated site-wide waste vector must be performed. This involves the following:

1. Defining a suitable time period as a basis for a consistent evaluation of the environmental impact. If a campaign mode of batch operation is assumed, then the cycle time $T$ is used; otherwise, the horizon time $H$ can be used instead.
2. Defining an emissions inventory comprising all wastes generated in any stage of the batch processing network within the global boundary of the batch plant of interest.
3. Grouping systematically these wastes in terms of the environmental damage caused (air pollution, water pollution, global warming, etc.). Ignoring pollution effects due to fate considerations, an Environmental Impact vector EI per time interval is defined to account for the fact that tasks generating waste do not operate continuously over time. Therefore, for each unit to task allocation, the indices which measure air pollution (CTAM, kg air), water pollution (CTWM, kg water), solid wastes (SMD, kg solids), global warming (GWI, kg $CO_2$), photochemical oxidation (POI, kg ethylene) and stratospheric ozone depletion (SODI, kg CFC11) are expressed for each waste $w$ emitted at time interval $t$, as shown in Fig. 8. Note that these metrics depend on the current legislation limits and the mass of pollutant disposed released (expressed as a proportion of the unit batch size).
4. Aggregating over time. For example, for cyclic operation, the cycle time $T$ is used as a basis for the quantification of global environmental impact GEI (if the batch plant does not operate on a cyclic mode then the environmental impact has to be aggregated over the required horizon time of production $H$).

$$\mathrm{GEI} = \sum_{t=1}^{T}\sum_{w=1}^{W} \mathrm{EI}_{\mathrm{wt}} = \sum_{t=1}^{T}\sum_{w=1}^{W} [\mathrm{CTAM}_{\mathrm{wt}}\mathrm{CTWM}_{\mathrm{wt}}\mathrm{SMD}_{\mathrm{wt}}\mathrm{GWI}_{\mathrm{wt}}\mathrm{POI}_{\mathrm{wt}}\mathrm{SODI}_{\mathrm{wt}}]^{T}_{\mathrm{process}}$$

**Example 2.** Multipurpose batch plants usually involve the production of several products where common resources are shared. When switching between products, or even after one

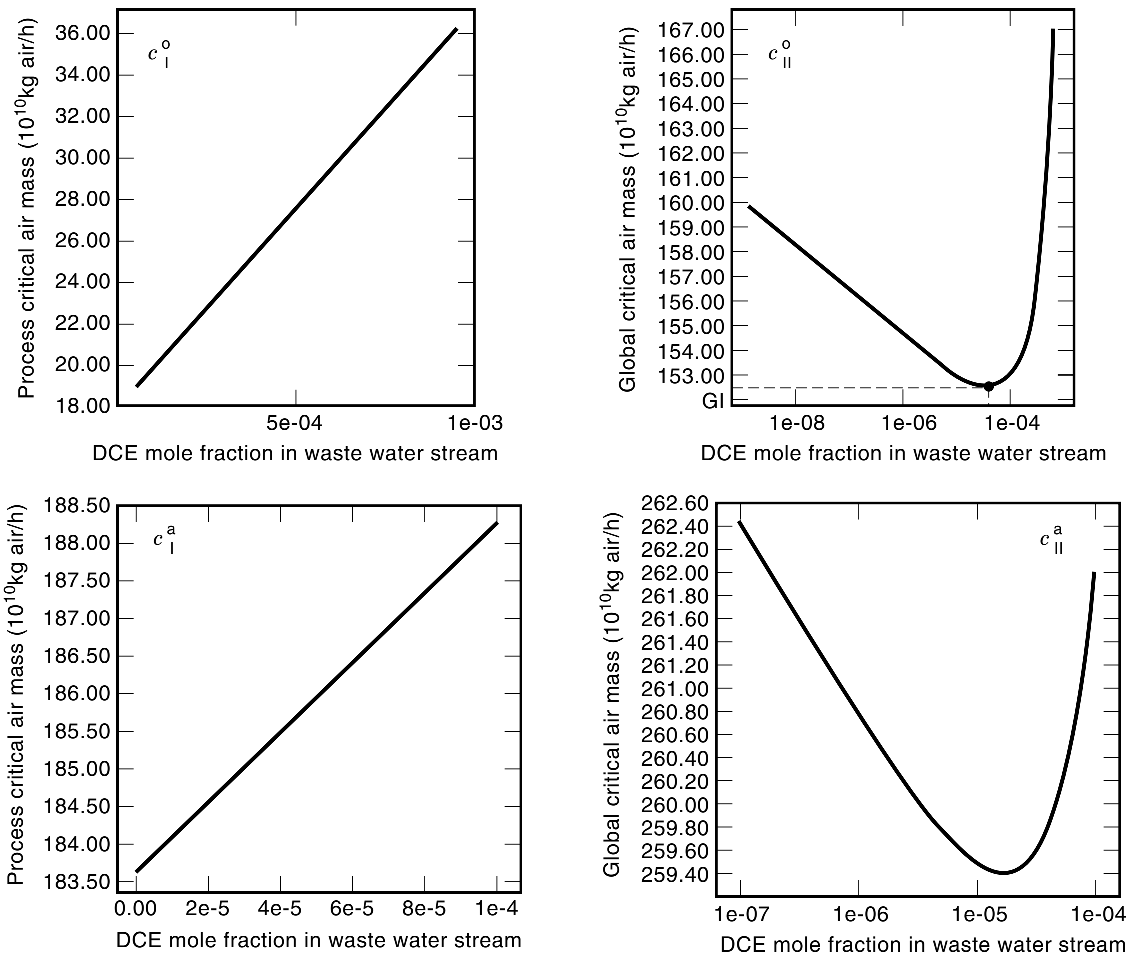


**Figure 15.** Effect of the degree of abatement on the optimal critical air mass impact of the DCE system (distillation case).

**Table 4. Optimal Operating Conditions of Process Alternatives with Minimum Global Critical Air Mass and Minimum Total Global Warming**

| Operating Conditions | Case $d_{II}^o$ | Case $f_{II}^o$ |
|---|---|---|
| Conversion of Hydrogen Chloride | 0.943 | 0.949 |
| Flash Drum Temperature (K) | 306 | 307.4 |
| Flash Drum Pressure (kPa) | 250 | 286.4 |
| Stripping Column Pressure (kPa) | 101.3 | 101.3 |
| Distillation Column II Pressure (kPa) | 202.5 | 204.1 |
| DCE mole fraction in waste water stream | $7 \times 10^{-6}$ | $9 \times 10^{-7}$ |
| CTAM (kg air/h) | $1.44 \times 10^{12}$ | $1.47 \times 10^{12}$ |
| GWI (kg $CO_2$/h) | 1594.3 | 1290 |

**Table 5. Comparison of Optimal Critical Air Mass (CTAM)**

| | From Process | Global |
|---|---|---|
| $d_I^o$ | $19 \times 10^{10}$ | $1.46 \times 10^{12}$ |
| $d_{II}^o$ | $16.2 \times 10^{10}$ | $1.44 \times 10^{12}$ |

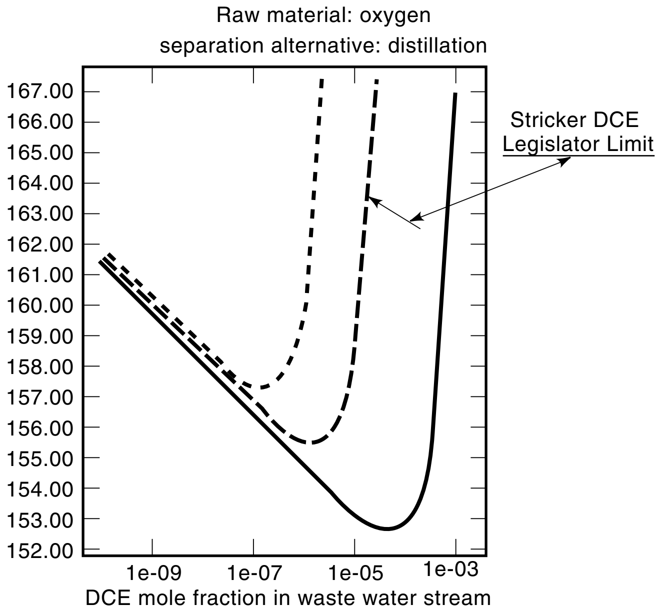


**Figure 16.** Effect of DCE legislation limit on the optimal global critical air mass impact.

or more batches of the same product, the equipment must often be cleaned for safety, product quality, and hygiene reasons. In many food and pharmaceutical plants, cleaning-in-place (CIP) stations must be included to flush detergents into many processing vessels. Cleaning cycles can be time consuming, and cleaning operations may affect the process schedule considerably. The wastes associated with cleaning constitute a major part of the overall environmental damage of a multiproduct batch plant and, therefore, the design and operation of the main batch process for minimum environmental impact should simultaneously address the design and operation problems of the cleaning stations required.

A multipurpose plant for the manufacture of two different types of cheese curd, namely low fat 0.8% w.t. Solcurd1 and high fat 1.27% w.t. Solcurd2, is employed to illustrate the potential of the methodology in addressing environmental issues involving task cleaning (Fig. 17). During processing, the reaction and draining vessels can become contaminated both microbiologically and by fouling deposit of proteins and minerals of whey by-product fluids. Cleaning with 100 kg of sodium hydroxide (NaOH) solution (the most common cleaning agent used in the dairy industry) is required after processing each batch of product. Cleaning experiments conducted for removal of whey protein soil deposits indicate that the required cleaning time CT (min), for 100% waste removal strongly depends on the temperature and the sodium hydroxide concentration $c_{N\alpha OH}$ (% w.t.) of the agent used; in particular, at 50 °C there is an optimal concentration of sodium hydroxide of 0.5% w.t., which results in the shortest cleaning time of 10 min; whereas concentrations of 2% w.t. NaOH increase the required time up to 45 min (40).

The CIP operation, as seen in Fig. 17, does not transform raw materials into useful products; rather it alters the state of process equipment from dirty to clean by preparing the detergent solution with desired properties (concentration, conductivity, and temperature). Although the cleaning operation consists of more than one task, like prerinsing, detergent cleaning, and final rinsing, in order to simplify the problem, all of the above can be aggregated in a single task with variable processing time. After cleaning, a large portion of the used detergent is recycled until the end of the cycle time and the remaining is stored in a disposal tank. The required task, unit and cost information is listed in Table 6.

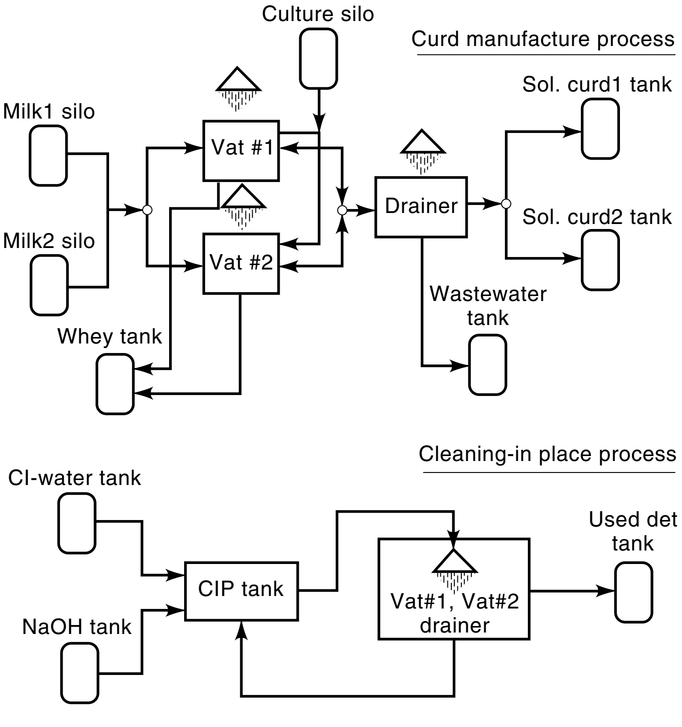


**Figure 17.** Multipurpose cheese curd production with cleaning-in-place.

In order to explore the implications of changing process design and sequencing on the environmental damage of the overall system, the proposed methodology is applied, and the main steps are illustrated below.

The expanded boundary in case of multiproduct cheese curd production is presented in Fig. 18.

Apart from the pollutants listed in Table 7, the emissions inventory now includes aqueous pollutants associated with cleaning (i.e., protein and other organics).

Cleaning constraints, so as to account for the case that specific tasks may change the state of a unit from clean to dirty and the effect of the cleaning-in-place process on the optimal sequencing and operation of a multipurpose batch plant, are included in the optimization formulation. The Mixed Integer Linear Programming problem was solved parametrically for various concentrations of the cleaning detergent. Regarding the environmental impact, major concern has been given to water pollution (quantified in terms of CTWM, kg water/cycle) since all process wastes generated involved aqueous effluents. The results are summarized as follows:

1. Cleaning considerations have a significant effect on both the cost and environmental impact of the process, since for each detergent concentration used, the required cleaning processing time is different. As it can be seen in Fig. 19, increased quantity of sodium hydroxide input to the process results in increase of global waste generation, since use of more concentrated detergent inherently implies more input waste from the NaOH production process. However, the trade-off among detergent concentration and cost is slightly more complicated; at low concentrations, the cleaning processing time (CT) decreases with concentration increase (40). This results in cost savings, since the probability of two cleaning tasks to occur simultaneously is smaller, and the used detergent recycling facility is fully utilized; as a consequence of this, the detergent requirements are lower, and the CIP tank volume is smaller. Figure 19 indicates that there is an optimal NaOH concentration of 0.5% w.t. above which the trend is reversed.
2. The importance of considering simultaneously the implications of design and scheduling on minimum environmental impact is another issue revealed in this example. The Pareto curve of solutions presented in Fig. 20 yields the family of schedules and designs that correspond to minimum cost while featuring minimum environmental impact in terms of CTWM. The effect of the operating policy on waste generation in multiproduct batch plants is significant. The optimal operating policy that corresponds to minimum annual cost [Fig. 21(a)]

**Table 6. Task Information, Unit Characteristics and State Cost Data for Example 2**

| Task | Duration (min) | In-Our State | In-Out Time (min) | In-Out Fraction |
|---|---|---|---|---|
| Vat Proc1 | 240 | I Culture | 0 | 0.12 |
| | | I Milk1 | 0 | 0.88 |
| | | O Whey | 240 | 0.896 |
| | | O Curd1 | 240 | 0.104 |
| Vat Proc2 | 240 | I Culture | 0 | 0.12 |
| | | I Milk2 | 0 | 0.88 |
| | | O Whey | 240 | 0.885 |
| | | O Curd2 | 240 | 0.115 |
| Drain1 | 30 | I Curd1 | 0 | 1.0 |
| | | O Solcurd1 | 30 | 0.9 |
| | | O Waste water | 30 | 0.1 |
| Drain2 | 30 | I Curd2 | 0 | 1.0 |
| | | O Solcurd2 | 30 | 0.9 |
| | | O Waste water | 30 | 0.1 |
| Cleaning | CT($c_{NaOH}$) | I Det for use | 0 | 1.0 |
| | | O Det for use | CT($c_{NaOH}$) | 0.99 |
| | | O Used Det | CT($c_{NaOH}$) | 0.01 |
| CIP Service | 30 | I ClWater | 0 | 1-$c_{NaOH}$ |
| | | I NaOH | 0 | $0.001 \leq c_{NaOH} \leq 0.02$ |
| | | O Det for use | 30 | 1 |
| Units | Suitability | Maximum Capacity (kg) | Fixed Costs (k£) | Variable Costs (k£/kg) |
| Vat 1 | Vat proc1, Vat Proc2 | 1100 | 75 | 0.45 |
| Vat 2 | Vat Proc1, Vat Proc2 | 1800 | 81 | 0.5 |
| Drainer | Drain1, Drain2 | 300 | 45 | 0.3 |
| Milk1,2 Silo | State Milk1,2 | 14100 | 15 | 0.1 |
| Culture Silo | State Culture | 10000 | 15 | 0.1 |
| CIP Tank | CIP Service | 10000 | 25 | 0.15 |
| Whey Tank | State Whey | 10000 | 15 | 0.1 |
| Waste Tank | State Waste | 10000 | 15 | 0.1 |
| SolCurd1,2 Tank | State SolCurd1,2 | 10000 | 15 | 0.1 |
| ClWater Tank | State ClWater | 10000 | 15 | 0.1 |
| NaOH Tank | State NaOH | 10000 | 15 | 0.1 |
| Used Det Tank | State Used Det | 10000 | 15 | 0.1 |
| State/Util. | Milk1,2 | SolCurd1,2 | ClWater | NaOH |
| Price (£/kg) | 0.16 | 0.655 | 0.002 | 0.001 |

yields a minimum cleaning time of 10 min and avoids parallel cleaning. Pollution prevention concerns have resulted in a minimum 0.04% increase of the annual cost by allowing the parallel cleaning of equipment and changing the cleaning time from 15 min to 45 min [Fig. 21(b)] but at the same time managing to reduce by 61% the amount of NaOH utilized.

## ENVIRONMENTAL IMPACT MINIMIZATION AND RISK ASSESSMENT OF NONROUTINE RELEASES

As discussed in the previous sections, the quantification of the environmental load in MEIM has been limited to routine release scenarios and, therefore, is unable to capture environmental degradation caused by unexpected events such as equipment breakdown, measurement errors, etc. A key characteristic of nonroutine releases is that they are related to equipment failures and the probabilistic occurrence of external events, such as unexpected leaks and human errors. As discussed earlier, in the hypothetical risk frequency graph presented in Fig. 3, nonroutine releases can significantly influence the environmental damage related to a process system. Unlike extreme cases such as major accidents (occurring at very low frequencies but with serious consequences) and routine releases (highly frequent but causing minor environmental damage), nonroutine releases, placed in between, often cause moderately severe adverse effects and may, therefore, result in considerable risk levels. This necessitates the development of an integrated framework that will properly account for nonroutine process waste generation due to unexpected/undesired events while simultaneously assessing the environmental impact of routine waste releases within the MEIM. Such a development will require quantitative means of translating waste emissions attributed to nonroutine releases to environmental impact indices, such as the ones presented earlier (for point source releases and/or long term effects). Since the environmental impact of a nonroutine release depends on its probability of occurrence, the machinery of reliability theory can be employed to provide such a formal link.

In the context of this work, environmental risk (ER) is the measure of potential threats to the environment taking into account that undesired events (scheduled/unscheduled) will lead to environmental degradation. Qualitatively, environmental risk represents the probability of environmental damage due to undesired events multiplied by the severity of the

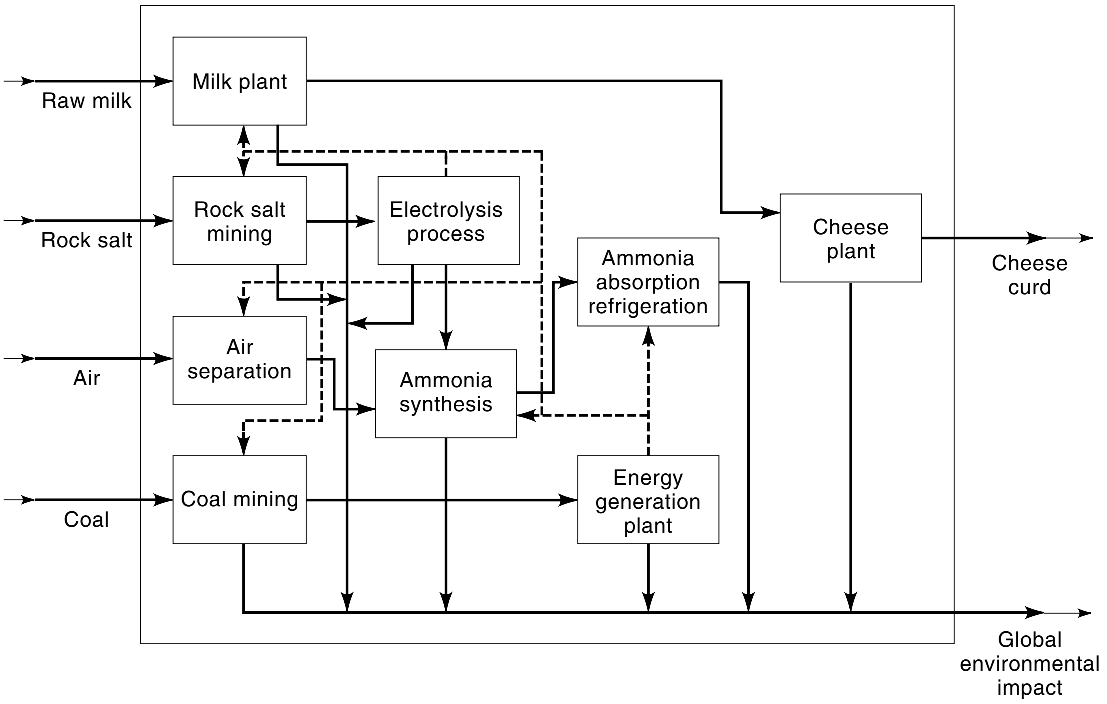


**Figure 18.** The global cheese curd production system.

**Table 7. Emissions Inventory for Example 2**

| | Air Pollutants | Water Pollutants | Solids |
|---|---|---|---|
| Curd Production | | BOD, COD, P, N, TSS | |
| Milk Standardization | | BOD, COD, P, N, TSS, TDS | |
| Energy Generation (incl. air separation and coal mining) | $CO_2$, CO, $CH_4$, RHC, RCHO Org, $NO_x$, $NO_2$, $SO_2$, dust | TDS, TSS, BOD COD, RCH, $NH_3$ | √ |
| AAR (incl. energy and ammonia synthesis) | Ar, $CO_2$, CO, $CH_4$, RCH, RCHO Org, $NO_x$, $NO_2$, $SO_2$, dust | TDS, TSS, BOD COD, RCH, $NH_3$ | √ |
| Electrolysis Process (incl. energy, salt mining) | Cl, Hg, $CH_4$, RCH, RCHO, Org $CO_2$, CO; $NO_x$, $NO_2$, $SO_2$, dust | Hg, TDS, TSS, BOD COD, RCH, $NH_3$ | √ |

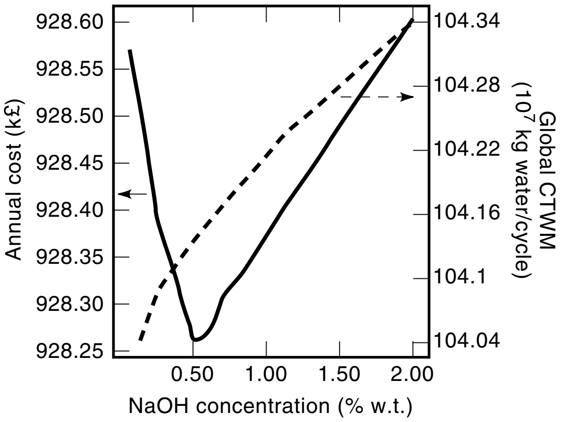


**Figure 19.** Effect of detergent concentration on environmental impact and cost.

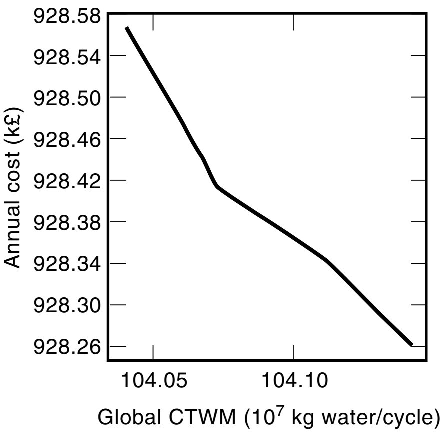
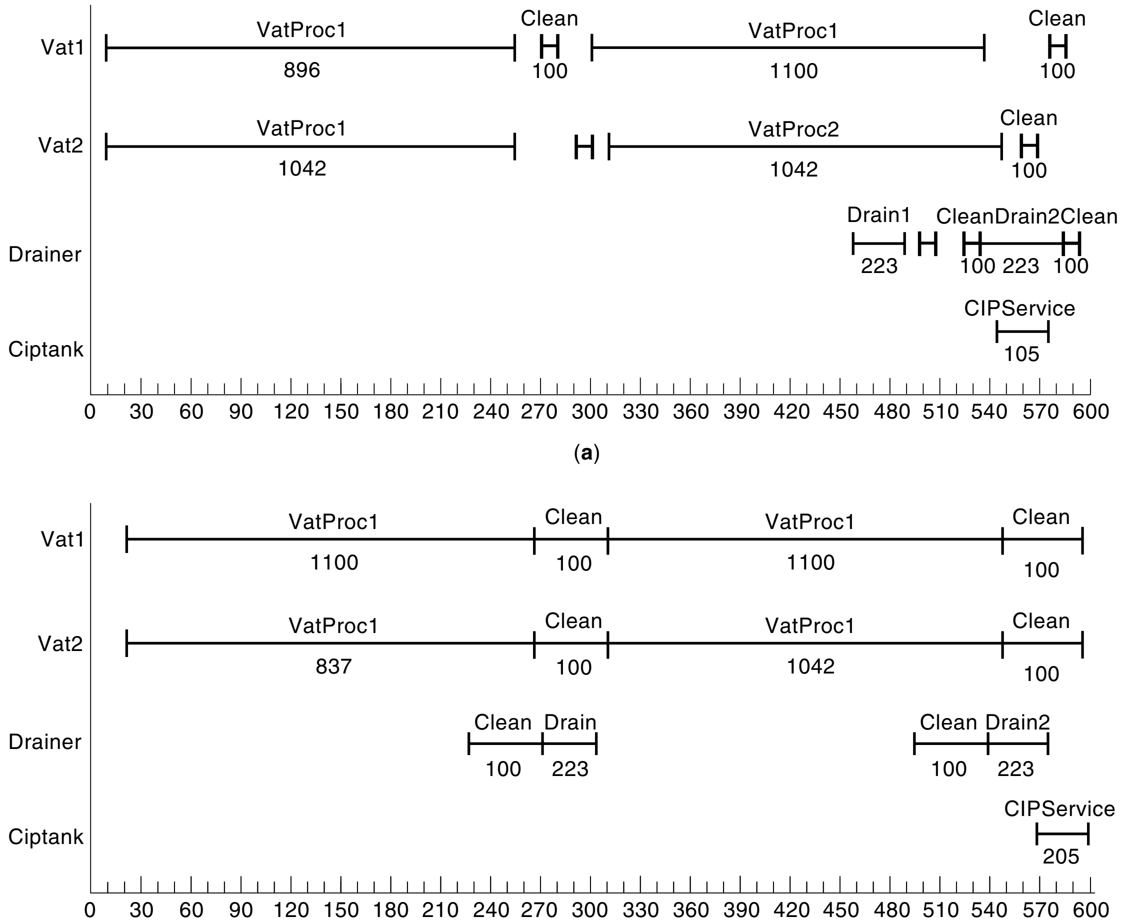


**Figure 20.** Pareto optimal curve for Example 2.



(**a**)

(**b**)

**Figure 21.** Optimal schedules for Example 2: (a) Gantt chart for min annual cost, (b) Gantt chart for min global *CTWM*.

environmental degradation. In accordance with the principles of MEIM, the system boundary around the process of interest is first specified. Concentrating mainly on process waste generation, the following framework for minimizing routine and non-routine releases is proposed (see Fig. 22).

### Routine and Nonroutine Emissions Inventory

The process of interest is examined in detail to determine

- Wastes that are regularly emitted into the air, aquatic or soil environment
- Various nonroutine releases such as
    1. *Accidental releases* mainly due to the occurrence of scenarios such as leakage, equipment failure, human error, etc.
    2. *Fugitive emissions* that involve small leaks or spills from pumps or flanges and are generally tolerated in industry
    3. *Releases from process deviations* caused during start-up, shut-down, maintenance procedures, and also from changes in operating conditions (temperatures, pressures) and various plant parameters such as feed variations
    4. *Episode releases* as a result of sudden weather changes or other occurrences

The overall inventory is represented by a waste vector, as shown in Fig. 22, which consequently needs to be assessed.

### Assessment of Environmental Damage

All routine and nonroutine releases are often grouped systematically in terms of the environmental damage caused on a short or long term basis. For the fully operable state (routine process system status), the EI vector shown below represents the damage caused to the environment during intended plant operation on a time basis (usually one hour of operation, ignoring pollutant intermedia partitioning), that is, the environmental impact of routine releases:

$$\mathrm{EI} = \sum_{w=1}^{W} \mathrm{EI}_w = \sum_{w=1}^{W} [\mathrm{CTAM}_w\ \mathrm{CTWM}_w \mathrm{SMD}_w\ \mathrm{GWI}_w\ \mathrm{POI}_w\ \mathrm{SODI}_w]^T_{\mathrm{process}} \quad (4)$$

When an equipment failure or an event which causes the system to significantly deviate from its normal operating status occurs, this defines a new operating state for which a corresponding environmental impact, similar to (4), can be then computed. This new operating state will also have an associated probability of occurrence which, in general, will be a function of equipment reliability models and other data (maintenance, safety events, statistical charts for spills, etc).

We denote the set of potential discrete operating states in which a process system can reside over its operating time horizon $H$ as state space $k$ with a corresponding probability $P^k(t)$, $k \in K$, where $t$ denotes time (since the reliability of the processing system is a function of time). A combined environmental impact vector for routine and nonroutine releases can then be introduced, CRNREI, to represent the average environmental damage of a given process design during normal and unexpected operation within a specified time horizon $[0, H]$ as follows.

### Algorithmic Procedure

**Step 1:** **(a)** Define all operating states $K$ of a process system using fault tree analysis principles; **(b)** Determine corresponding environmental impact vector ($\mathrm{EI}^k$), $k \in K$

**Step 2:** **(a)** Estimate the reliability (unavailability) of each part of the equipment as a function of time, $R_j(t)$ [$Q_j(t)$]. For example, if Weibull functions are used to describe equipment reliability,

$$R_j(t) = \int_t^{\infty} weif\left(\frac{t}{\alpha_j}; \beta_j\right) dt, \quad j \in S_k \quad Q_j(t) = \int_0^t weif\left(\frac{t}{\alpha_j}; \beta_j\right) dt, \quad j \in \overline{S_k} \tag{5}$$

where $S_k(\overline{S}_k)$ is the index set for operational (failed) components of the equipment in state $k$, and $\alpha$, $\beta$ are the scale and shape factor of the Weibull function. **(b)** Determine the probability of each state $k$, for example, assuming statistically independent equipment failures:

$$P^k(t) = \prod_{j \in S_j} R_j(t) \prod_{j \in \overline{S_j}} Q_j(t) \qquad k \in K \tag{6}$$

**Step 3**: Calculate the Environmental Impact Vector as a function of time, $EI(t)$:

$$\mathrm{EI}(t) = \sum_{k \in K} P^k(t)\mathrm{EI}^k \tag{7}$$

**Step 4:** Determine the combined Environmental Impact of Routine and Nonroutine releases for a given time horizon $H$.

$$\mathrm{CRNREI} = \frac{1}{H}\int_H \mathrm{EI}(t)\,dt = \frac{1}{H}\int_H \sum_{k \in K} P^k(t)\mathrm{EI}^k \tag{8}$$

Qualitatively, this vector represents the minimum average environmental impact of the process design over all possible system states within a specified time horizon $H$. Therefore, it measures the average system environmental performance under both expected and unexpected events. The closer this vector is to the Environmental Impact vector of the initial state (denoted here as fully operable state $o$), the lower environmental risk the system conveys.

Note that the Environmental Impact vector corresponding to Nonroutine releases, NREI, over the time horizon can be easily computed as follows:

$$\mathrm{NREI}^k = \mathrm{EI}^k - \mathrm{EI}^o \quad k \in K \tag{9}$$

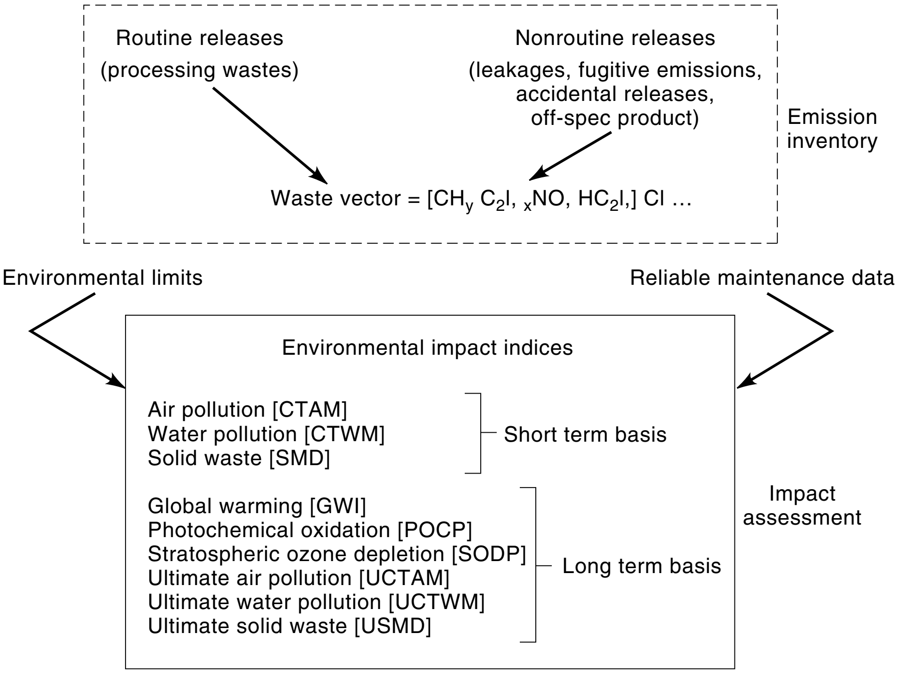


**Figure 22.** Environmental impact assessment of routine/nonroutine releases.

where $\mathrm{EI}_o$ is the Environmental Impact metric corresponding to the fully operable state; that is, it denotes routine waste releases.

$$\mathrm{NREI}(t) = \sum_{k\in K} P^k(t)\mathrm{NREI}^k \tag{10}$$

$$\mathrm{NREI} = \frac{1}{H}\int_H \mathrm{NREI}(t)\,dt = \frac{1}{H}\int_H \sum_{k\in K} P^k(t)\mathrm{NREI}^k\,dt \tag{11}$$

Qualitatively, NREI represents the average environmental impact due to nonroutine releases. For the fully operable state, NREI = 0, as expected.

### Design Optimization for Minimum Environmental Impact and Environmental Risk

The combined environmental impact vector, as stated above, provides an accurate estimate of the average environmental performance of the system taking into account both routine and nonroutine releases. In the analysis presented so far, decisions regarding the process design itself (for example, volumes of equipment) were considered fixed. A subsequent question is, then, how to obtain a minimum cost design while ensuring that the system is capable enough of keeping routine and non-routine release levels as low as possible. Conceptually, this problem can be posed as the following multiobjective optimization problem. Revisiting Eq. (2),

$$\min_{x,y}[c^T y + f(x),\ \mathrm{CRNREI}] \tag{12}$$

s.t.

$$h(x) = 0$$
$$g(x) \le 0$$
$$A\cdot x = a$$
$$B\cdot y + C\cdot x \le d$$
$$\mathrm{CRNREI}(x,y) = \frac{1}{H}\int_H \sum_{k\in K} P^k(t)\mathrm{EI}^k\,dt$$
$$\mathrm{NREI}(x,y) = \frac{1}{H}\int_H \sum_{k\in K} P^k(t)(\mathrm{EI}^k - \mathrm{EI}^o)\,dt$$
$$x\in X, y\in Y$$

Equation (12) can be reformulated using the $\epsilon$-constraint method:

$$\min_{x,y} c^T y + f(x) \tag{13}$$

s.t.

$$h(x) = 0$$
$$g(x) \le 0$$
$$A\cdot x = a$$
$$B\cdot y + C\cdot x \le d$$
$$\mathrm{NREI}(x,y) = \frac{1}{H}\int_H \sum_{k\in K} P^k(t)(\mathrm{EI}^k - \mathrm{EI}^o)\,dt$$
$$\mathrm{CRNREI}(x,y) \le \epsilon$$
$$x\in X, y\in Y$$

**Solution Procedure.** Based on the following assumptions:

- Steady state process and environmental (considering either point source or pollutant fate behaviour) models are used
- Individual components reside in either an operable or failed state
- All events are statistically independent
- Reliability data are available as functions of time for equipment failures and all external events

an iterative procedure is proposed, to overcome the above difficulty, based on a modified Generalised Benders Decomposition (41) scheme as can be seen in Fig. 23.

By fixing the design variables, CRNREI is estimated for the plant's feasible operating region (all feasible system states) via the solution of an optimisation problem. A master problem is then constructed for updating the design variables, while trade-off considerations between cost and CRNREI or NREI are taken into account.

### Environmental Risk Implications for Maintenance

Having identified the most environmentally benign yet economically optimal design with respect to all sorts of release scenarios, the idea of criticality analysis (42) can then be applied to identify and rate the most critical events with respect to plant performance and the environment. More specifically, we are interested in the sensitivity of environmental risk NREI(t) to the probability of an event $l$, $\rho_{l^*}$. Then,

$$\mathrm{NREIC}_{l^*}(t) = \frac{\partial\mathrm{NREI}(t)}{\partial r_{l^*}} = \sum_{k\in K}\left\{\mathrm{NREI}^k \frac{\partial P^k(t)}{\partial r_{l^*}}\right\} \tag{14}$$

since the estimation of $\mathrm{NREI}^k$ is not influenced by $\rho_{l^*}$.

Note that based on the above algorithm, equipment/events can be ranked according to their corresponding criticality index. Exact details of the above analysis and an algorithm to facilitate its application are described in (42). The results from such a ranking can be then used as guidelines for maintenance and environmental optimization given the following:

- Maximum allowable environmental risk target values ($\mathrm{NREI}^T$),
- Quantitative information regarding maintenance resources (number of service crews, job durations etc.) and tasks (equipment maintenance specifications, list of scheduled preventive maintenance activities).

The designer can explore opportunities for maintenance execution based on a formal assessment of the deterioration of the operating and, hence, environmental system performance over time and the relative effect of restoring the performance of critical equipment on the environmental damage caused by unintended emissions. Although details of the preventive maintenance algorithm are given elsewhere (43), it should be pointed out that the environmental risk implications for maintenance identified in this work rely on the assumptions that (1) unlike reliability, environmental impact measures do not change with respect to time, (2) equipment is either main-

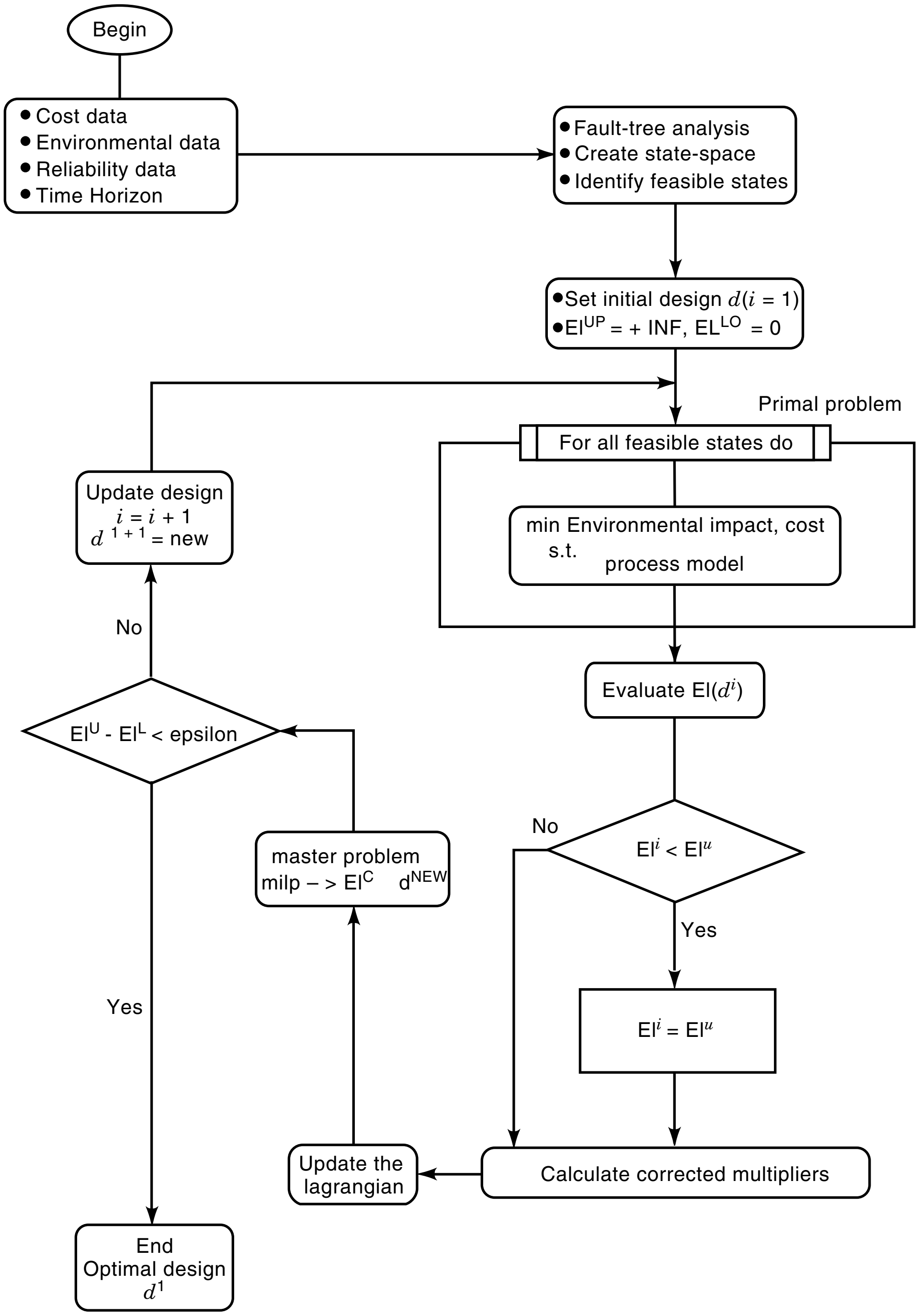


**Figure 23.** Algorithm for design optimization.

tainable or unmaintainable, (3) after maintenance, each equipment is considered "as good as new," (4) during the maintenance period there is no significant waste disposal, (5) continuous plant operation is considered, and (6) ordering of maintenance tasks is based on the equipment environmental criticality (that is, the most critical equipment with respect to NREI is maintained first).

**Example 3.** Consider the simplified chloromethane reaction subsystem (44) shown in Fig. 24. Chloromethanes are produced according to the following reaction scheme:

$$\begin{aligned} CH_4 + Cl_2 &\rightarrow CH_3Cl + HCl \quad &[RXN1]\\ CH_3Cl_2 &\rightarrow CH_2Cl_2 + HCl \quad &[RXN2]\\ CH_2Cl_2 + Cl_2 &\rightarrow CHCl_3 + HCl \quad &[RXN3]\\ CHCl_3 + Cl_2 &\rightarrow CCl_4 + HCl \quad &[RXN4] \end{aligned}$$

that takes place in the gas phase with chlorine as the limiting reactant. The design must be such that chlorine is not allowed to accumulate in large quantities in the reaction system due

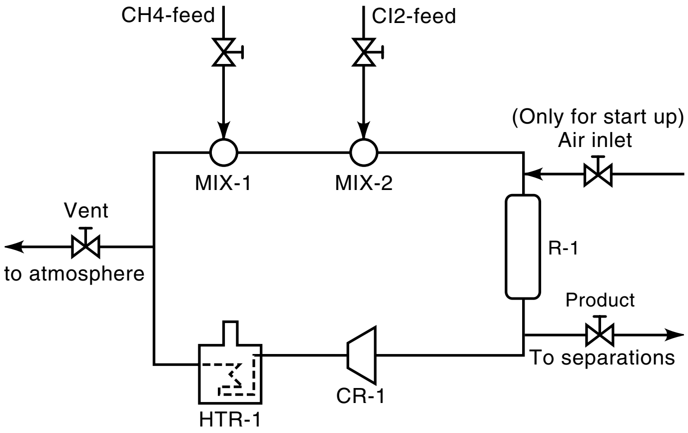


**Figure 24.** Simplified chlorination flowsheet.

to explosion hazards; therefore, it should not exceed a specified stoichiometric amount with respect to methane reactor feed. The system is equipped with vents to the atmosphere and also to the separation system which is not included in this case for simplicity. There is an air feed line that is open when the system is not operating. Pressure effects are negligible, and the reactor operates at 3 atm. A two stage recycle compressor with intercooler is required which is assumed to operate adiabatically, followed by a gas fired heater to ensure that the inlet reactor gases are partially preheated by the recycle gases to reach a sufficiently high temperature to minimize heat control problems. While the kinetics of the reaction scheme are given in detail elsewhere (34), the following operating constraints need to be satisfied for inherently safe operation in order to produce a stream of 50 kgmols/h to be fed directly to the separation block:

$$400 \leq \text{Reactor Temperature}(^\circ\text{C}) \leq 457$$

$$\text{Air Feed} = 0$$

$$\text{Chlorine to Methane Molar Feed Ratio} \leq 3$$

Temperatures much above 450°C cannot be tolerated since pyrolysis would occur. Pyrolysis is a very exothermic reaction and once initiated, quickly reaches explosive violence. Presence of oxygen in the system decreases the rate of the reaction (1.25% wt oxygen in the reactor feed decreases approximately two fold the rate of chlorination at the studied temperature range) as it behaves as an inhibitor. High chlorine to methane molar feed ratios result in the accumulation of large amounts of chlorine in the system which may lead to explosion; for this reason, material input flowrates are adjusted so that the chlorine to methane molar ratio at the inlet of the reactor has a value of 1.3.

Most of the process equipment is highly reliable apart from (1) the recycle compressor system which has a performance described by a Weibull function and (2) the measuring devices monitoring the ratio of chlorine to methane fed to the reactor, the air feed flow, and the reaction temperature. The measurement errors are regarded as discrete events, and as their probability drifts with respect to time, they are described by an exponential density function of the following form:

$$f(t) = \lambda \exp(-\lambda t) \tag{15}$$

In addition, the exponential distribution model is used to describe the probability of occurrence of external events such as gaseous leaks from the recycle piping system that have occurred in the past. Table 8 summarizes the required reliability data for each event.

The following environmental data (34,21) are also supplied for the process of interest:

| Chemical | Maximum Acceptable Concentration (kg/tn air) | Global Warming Potential (kg $CO_2$/kg pol.) |
|---|---|---|
| $Cl_2$ | $1.67\ 10^{-5}$ | — |
| $CH_4$ | 0.0125 | 11 |
| $CH_3Cl$ | $8.333\ 10^{-6}$ | 5 |
| $CH_2Cl_2$ | $8.333\ 10^{-6}$ | 15 |
| $CHCl_3$ | $8.333\ 10^{-6}$ | 25 |
| $CCl_4$ | $8.333\ 10^{-6}$ | 1300 |
| HCl | $8.333\ 10^{-5}$ | — |
| $O_2$ | — | — |

**System Boundary and Emissions Inventory.** The system boundary is considered around the methane chlorination process, and therefore, the emissions inventory consists mainly of chlorinated hydrocarbons, unreacted raw materials, and byproducts vented to the atmosphere:

$$\text{Waste Vector} = [Cl_2CH_4CH_3ClCH_2Cl_2CHCl_3CCl_4HClO_2]_{\text{process}}$$

**Environmental Impact Assessment of Routine and Nonroutine Releases.** The waste vector defined above is aggregated into an environmental impact vector of low dimensionality, reflecting the actual damage caused to the environment. In this case, the metrics employed to investigate the routine/nonroutine environmental behaviour of the process are

$$\text{EI} = [\text{CTAM GWI}]^T_{\text{process}} \tag{16}$$

and depend on the mass of pollutant discharged, the maximum acceptable concentration limits, and the global warming potentials defined by the user (see earlier).

The probability of the system degrading into a nonoperable state is negligible, since mixers, inlet valves, and the reactor are fully reliable. The external events are all assumed to cause degradation to operable states with decreased reliabil-

**Table 8. Reliability Data for Example 3**

Horizon, $H = 4$ yr

CR-1 $\alpha = 120000$ 1/h $\beta = 1$ MTTR = 72 h

| Event | $ERR_{Cl2:CH4} = +8\%$ | $ERR_{TREA} = +5\%$ | 1 MM Leak | 3 MM Leak | $F_{O_2} = 0.1$ kgmol/h |
|---|---|---|---|---|---|
| $\lambda$(1/h) | $3\ 10^{-6}$ | $5\ 10^{-6}$ | $1\ 10^{-5}$ | $4\ 10^{-6}$ | $1\ 10^{-6}$ |

**Table 9. System Degraded States for Example 3**

| State $k$ | $\mathrm{ERR}_{\mathrm{Cl2:CH4}}$ = 8% | $\mathrm{ERR}_{\mathrm{TREA}}$ = 5% | 1 mm Leak | 3 mm Leak | $F_{\mathrm{O}_2}$ = 0.1 kgmol/h | CR-1 fails |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | √ | | | | | |
| 3 | | √ | | | | |
| 4 | | | √ | | | |
| 5 | | | | √ | | |
| 6 | | | | | √ | |
| 7 | | | | | | √ |
| 8 | √ | √ | | | | |
| 9 | √ | | √ | | | |
| 10 | √ | | | √ | | |
| 11 | √ | | | | √ | |
| 12 | √ | | | | | √ |
| 13 | | √ | √ | | | |
| 14 | | √ | | √ | | |
| 15 | | √ | | | √ | |
| 16 | | √ | | | | √ |
| 17 | | | √ | | √ | |
| 18 | | | | √ | √ | |
| 19 | | | | | √ | √ |
| 20 | √ | √ | √ | | | |
| 21 | √ | √ | | √ | | |
| 22 | √ | √ | | | √ | |
| 23 | √ | √ | | | | √ |
| 24 | √ | | √ | | √ | |
| 25 | √ | | | √ | √ | |
| 26 | | √ | √ | | √ | |
| 27 | | √ | | √ | √ | |
| 28 | | √ | | | √ | √ |
| 29 | √ | √ | √ | | √ | |
| 30 | √ | √ | | √ | √ | |
| 31 | √ | √ | | | √ | √ |

ity and therefore, according to Table 9, the operable degraded system states number 31. The state probability estimation indicates that (1) a 1 mm leak on the recycle is more likely to occur than any other undesired event, (2) all external events have greater probabilities of occurrence than failure of CR-1, and (3) simultaneous occurrence of more than two undesired events is most rare.

**Optimization for Minimum Environmental Risk.** The optimization problem is posed as explained earlier; the design variable to be optimized is the volume of the reactor $V_R$ ($1.5 \leq V_R(\mathrm{m}^3) \leq 3$), and the degrees of freedom for each operable state are listed below:

$$675 \leq \text{Nominal reactor temperature (K)} \leq 730$$

$$0.2 \leq \text{Recycle to separations molar ratio} \leq 0.971$$

$$900 \leq \text{Heater outlet temperature (K)} \leq 1200$$

The results summarized in Table 10 reveal some interesting points:

- Cost optimization yields a smaller reactor (2.44 $\mathrm{m}^3$) but at the same time results in substantially increased global warming impact due to non-routine releases.
- By minimizing the expected value of critical air mass, reduction of environmental risk $\mathrm{NREI}_{\mathrm{CTAM}}$ can be achieved in the order of 8%, compared to the corresponding cost optimal value (see Table 10). In addition, environmental risk related to global warming is reduced by almost 33%. However, one has to pay an economic penalty for pollution reduction in this case, as optimization of $\mathrm{CRNREI}_{\mathrm{CTAM}}$ has a negative effect on the economics of the process (30% increase in cost).
- As can be seen in Table 10, optimization of $\mathrm{CRNREI}_{\mathrm{GWI}}$ yields the most interesting results since the contribution

**Table 10. Summary of Results for Example 3**

| | min Expected COST | min $\mathrm{CRNREI}_{\mathrm{CTAM}_\mathrm{H}}$ | min $\mathrm{CRNREI}_{\mathrm{GWI}_\mathrm{H}}$ |
|---|---|---|---|
| Annual cost (M$) | 195225 | 253540 | 209670 |
| $\mathrm{NREI}_{\mathrm{CTAM}_\mathrm{H}}$ ($10^6$ kg air/h) | 2622 | 2414 | 2630 |
| $\mathrm{NREI}_{\mathrm{GWI}_\mathrm{H}}$ (kg $\mathrm{CO}_2$/h) | 12878 | 8612 | 2445 |
| $V_\mathrm{R}$ ($\mathrm{m}^3$) | 2.44 | 2.6 | 2.49 |

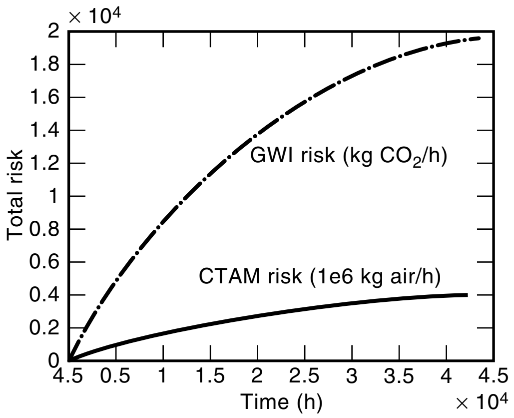


**Figure 25.** Environmental risk response with respect to time.

of nonroutine releases with respect to global warming is reduced six fold! At the same time, the annual cost and the critical air mass are maintained at low levels, and the optimal reactor design is quite similar to its cost optimal.

- The dynamic response of environmental risk NREI(t), corresponding to the cost optimal case, is presented in Fig. 25 and shows that both GWI and CTAM risks increase with respect to time as the reliability of the system decays. Note that both environmental metrics are based on steady state environmental behaviour of pollutants and, in the context of this work, the time dependence is a result of the reliability analysis. The time averaged integral of the dynamic response results in the risk values presented in Table 10.
- Figures 26 and 27 demonstrate the deviation of the environmental impact metrics CTAM and GWI, respectively, from their fully operable state values for each of the 31 degraded states. As can be observed from both graphs, failure of CR-1 (states 7,12,16,19,23,29,31) results in significantly increased damage in every case. The following trends can also be revealed concerning CTAM (see Fig. 26): (1) the air pollution damage that corresponds to optimization of $\mathrm{CRNREI}_{\mathrm{CTAM}_H}$ is consistently less for each state apart from state 2 (measurement error in molar feed ratio of reactants), verifying the fact that total CTAM is optimal in this case, and (2) minimization of $\mathrm{CRNREI}_{\mathrm{GWI}_H}$ results in larger CTAM in states above $k = 22$; the overall CTAM, though, does not increase significantly because of their low probability of occurrence. Figure 27 shows that GWI deviation is less in almost every state in case of $\mathrm{CRNREI}_{\mathrm{GWI}_H}$ minimization but is significantly greater when expected CTAM is minimized (see states 10, 27, 28)! Therefore, global warming optimization seems to be a better compromise solution with respect both to cost and critical air mass.

**Environmentally Critical Equipment and Preventive Maintenance Policy.** In order to detect the process bottlenecks with respect to environmental risk, a criticality analysis is performed with respect to the environmental impact vector of NREI. The criticality index rNREIC, presented in Table 11, demonstrates that failure of the recycle compressor is the main bottleneck of the process, as it has the largest effect on environmental damage, followed by the leaks on the recycle and, finally, the measurement errors. The preventive maintenance policy followed to satisfy $\mathrm{NRREI}_{\mathrm{GWI}}(t) \leq 1000$ kg $CO_2$ is presented in Fig. 28. The equipment maintenance policy dic-

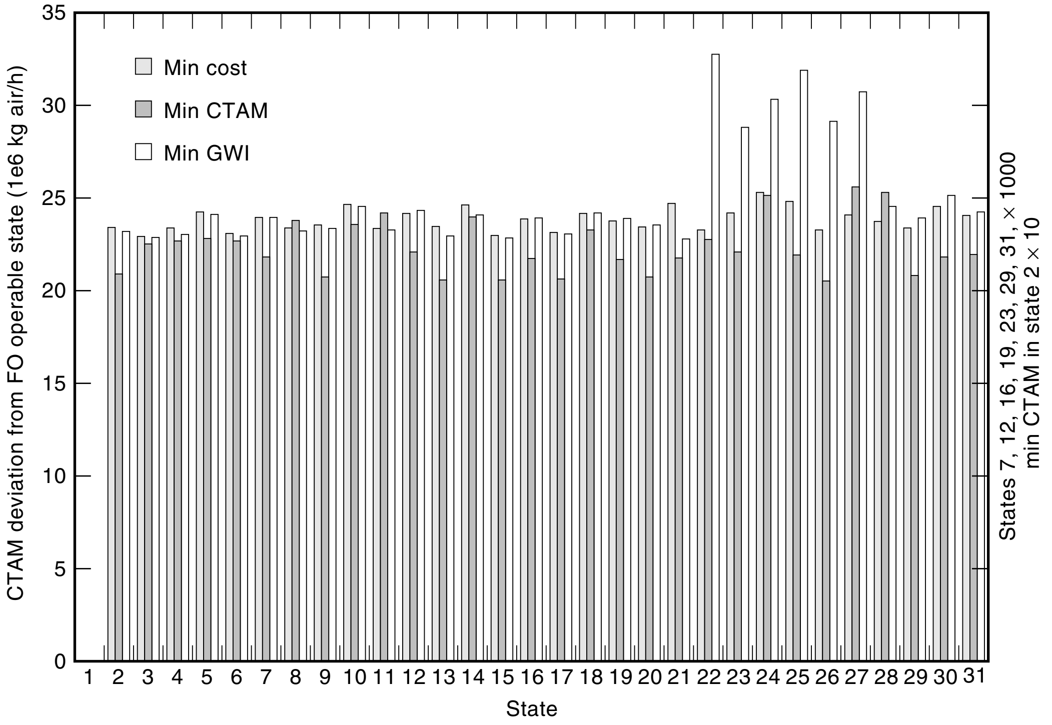


**Figure 26.** CTAM deviation from fully operable case for each degraded state.

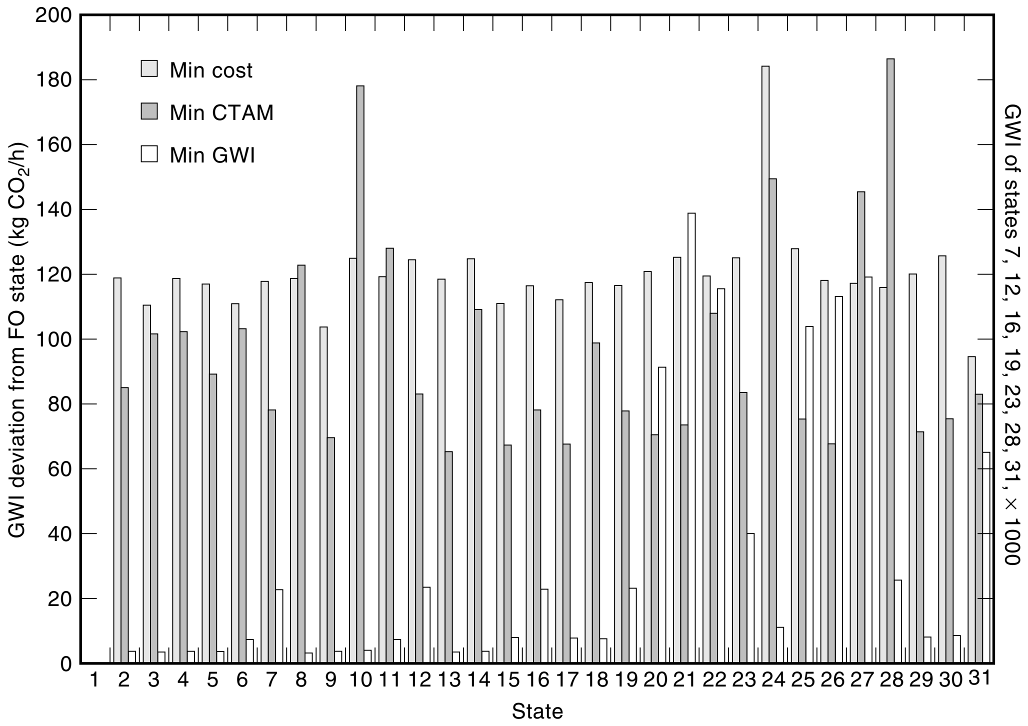


**Figure 27.** GWI deviation from fully operable case for each degraded state.

tates that CR-1 must be maintained every 5000 h of operation.

**Table 11. Criticality Index of Equipment Failures for Example 3**

| Event | $r\mathrm{NREIC}_{t=0}$ | $r\mathrm{NREIC}_{t=1\mathrm{yr}}$ |
|---|---|---|
| CR-1 fails | 1 | 1 |
| 3 mm Leak | 0.001 | 0.076 |
| 1 mm Leak | 0.001 | 0.072 |
| $\mathrm{ERR}_{\mathrm{Cl2:CH4}} = +8\%$ | 0.001 | 0.001 |
| $F_{O_2} = 0.1$ kgmol/h | 0.001 | 0.001 |
| $\mathrm{ERR}_{\mathrm{TREA}} = +5\%$ | 0.001 | 0.001 |

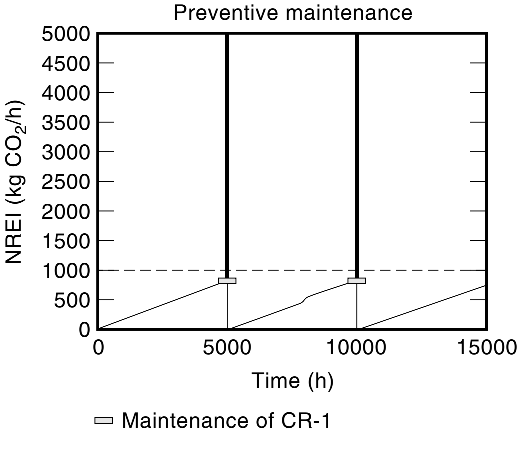


**Figure 28.** $\mathrm{NRREI}_{\mathrm{GWI}}$ response and maintenance policy for minimum global warming.

## CONCLUSIONS

This article considers the incorporation of life cycle aspects in the synthesis and design of process systems. Generic tools for the quantitative assessment and optimization of the full range of environmental impacts associated with the manufacture of a given product are proposed.

In particular, a methodology is introduced which involves the development of formal environmental impact analysis tools and their systematic integration with mathematical programming based process synthesis techniques to address various aspects of waste reduction and prevention at source, including alteration of process units, operating conditions, and policies to reduce the generation of undesirable pollutants. Life cycle analysis principles are used for the assessment of the macroscopic consequences of pollution prevention, and formal reliability techniques are employed to tackle environmental problems related to unintentional plant operation. The basic steps of the integrated framework feature

- Determination of a consistent boundary around the process of interest to identify input wastes to the system (for example, due to energy, raw materials consumption) as well as output waste generation (such as air emissions, wastewaters, etc.)
- Quantification of the full range of adverse environmental effects of a process, including aspects of point source as well as post-release pollutant behavior and damage related to both routine releases and unexpected events due

to process degradation (such as equipment failures, leaks, etc.)
- A multiobjective optimization formulation to formally establish the trade-offs between cost and different quantitative metrics of pollution (such as routine/non-routine air, water pollution, global warming, etc.) and identify the family of designs, operating conditions, and material alternatives that minimize environmental damage without entailing excessive cost (best practical environmental option, BPEO) for continuous and batch processes
- An analytical method to detect environmental risk process bottlenecks and identify maintenance opportunities to increase environmental quality

A number of detailed example problems have been presented to illustrate the potential of the proposed methodology.

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**LIFELONG LEARNING.** See Continuing education.