METHODOLOGY FOR THE DESIGN OF ECONOMICAL AND ENVIRONMENTAL FRIENDLY PROCESSES: AN UNCERTAINTY APPROACH

By

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Mauricio Dantus

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NOMENCLATURE

Roman letters

a	Temperature exponent
A	Pre-exponential factor
A_f	Annuity factor
Ap	Annual operating costs
Au	Annual cost of utilities
b	Concentration exponent
b_0	Weighting function constant
C	Capital cost
$C_{A/B}$	Chemical is known or is probable to be a human carcinogen
C_C	Chemical is possible to be a human carcinogen
C_{FC}	Fixed capital investment
c_j	Cost of component j
c_L	Percentage of the claims that require compensation payments
C_L	Cost of land and other non-depreciable costs
Cn	Concentration
C_{PE}	Purchased equipment costs
C_{TC}	Total fixed capital investment

C_{WC}	Working capital
D_j	Disposal cost
d_j	Distance to waste treatment or disposal facility
E_a	Activation energy
$E(x)$	Expected value of x
f	Flowrate (kg/hr)
F	Cash flow
f_D	Depreciation factor
f_H	Frequency of occurrence per year
f_i	Inflation factor
$f(x)$	Probability density function
G	Number of units away from the average value
$g(\,)$	Set of equality constraints
$h(\,)$	Set of inequality constraints
h	Henry's constant
HV_x	Hazard value of endpoint x
H_x	Expenses of item x
i	Index value
i_f	Annual inflation rate
i_r	Interest rate
I_0	Initial investment
I_D	Depreciable investment
j	Compromise index

k	Constant that governs the rate of increase
k_B	Boltzmann constant
k_c	Compensation costs incurred in the event of a claim given a release
k_f	Fines and/or penalties for non-compliance of an environmental regulation
k_N	Natural resource damage expenses to be paid in the event of a release
k_r	Remediation costs incurred in the event of a release
L	Lower value of continuous variable
L_c	Legal defense costs
L_j	Distance from the ideal point
m_H	Non-labor costs
M_i	Transportation cost to waste treatment or disposal facility
$m_{j,i}$	Mass fraction of component j in waste stream i
M_L	Markov chain length
n	Number of years
N_o	Number of operators
n_s	Sample size
Ny	Project's lifetime
P	Product flowrate (kg/hr)
Q	Plant or equipment capacity
r	Release factor
R	Universal gas law constant
RfC	Chronic reference concentration (mg/m^3)

RfD	Chronic reference dose (mg/kg-day)
s	Shift earning per hour
S_C	Sample size for continuous variable
SF	Oral slope factor (risk per mg/kg-day)
S_j	Societal or damage cost
S_s	Number of samples step size
ST	Storage time
s_x	Sensibility index
S_v	Salvage value
t	Time required (hours per occurrence)
T	Temperature
Tr_i	Treatment cost
Tx	Tax rate
u	Payoff value
U	Upper value of continuous variable
UR	Inhalation unit risk (risk per mg/m^3)
v	Rate of reaction
W	Direct waste cost
w_i	Flowrate of waste stream i (kg/hr)
$\mathbf{x}$	Vector of continuous variables
$\mathbf{y}$	Vector of discrete variables
z	Objective function
$Z(T)$	Partition function

Greek letters

α	Direct cost correction factor
α_T	Temperature function constant
β	Indirect cost correction factor
Φ	Environmental impact index of chemical j (EIU/kg)
γ	Preference weight
θ	Environmental impact (EIU/kg)
σ	Standard deviation
Ω	Vector of uncertain variables
ψ	Exponent

Subscripts

0	Original value
e	Existing process
n	New process
p	Value at present time

Mathematical symbols

$\wp(x)$	Probability of x

Abbreviations

AEP	Annual equivalent profit
ARB	Average return on book value

ATTIC	Alternative Treatment Technology Information Center
BOD	Biochemical Oxygen Demand
CAA	Clean Air Act
CE	Chemical Engineering Plant Cost Index
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CP	Compromise programming
CWA	Clean Water Act
DPB	Discounted payback period
DMU	Decision making unit
EIU	Environmental impact units
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
EVA	Economic value added
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FW	Future worth
HAP	Hazardous air pollutants
HEN	Heat exchanger network
HSWA	Hazardous and Solid Waste Amendments
InRR	Incremental rate of return
IRR	Internal rate of return
IRRI	Internal rate of return index
IRRM	Internal rate of return margin
ISO	International Organization for Standardization

LOAEL	Lowest level at which an adverse effect is observed
M&S	Marshall and Swift Equipment Cost Index
MACT	Maximum available control technology
MACRS	Modified Accelerated Cost Recovery System
MARR	Minimum attractive rate of return
MEN	Mass exchanger network
MINLP	Mixed integer non linear programming
MOOP	Multiple objective optimization problem
MOSO	Multiple objective stochastic optimization
NOAEL	Highest level at which no adverse effect is observed
NPDES	National Pollutant Discharge Elimination System
NPF	Net payout fraction
NPV	Net present value
NRR	Net return rate
OECD	Organisation for Economic Co-operation and Development
ORR	Overall rate of return
OSHA	Occupational Safety and Health Act
PB	Cash payback method
PCB	Polychlorinated biphenyl
PI	Profitability index
PIR	Profit to investment ratio
PP	Payout period
PPI	Payout period including interest

PPIC	Pollution Prevention Information Clearinghouse
PPP	Polluter Pays Principle
PWP	Premium worth percentage
QSARs	Quantitative structure-activity relationships
RCRA	Resource Conservation and Recovery Act
REVA	Refined economic value added
RMP	Risk management program
ROR	Rate of return on investment
RTK	Right-to-Know
SA	Stochastic annealing
SARA	Superfund Amendments and Reauthorization Act
SCF	Specific chemical flowsheet
SDWA	Safe Drinking Water Act
SOOP	Single objective optimization problem
SQP	Successive quadratic programming
TCA	Total cost assessment
TRI	Toxic Release Inventory
TSCA	Toxic Substances Control Act
TVM	Time value of money
VOC	Volatile organic compounds

CHAPTER 1

INTRODUCTION

The process industry is responsible for the generation of large amount of wastes including hazardous and non-hazardous wastes. To manage these wastes, the most common approach has been to employ end-of-the-pipe treatment technologies that try to reduce or eliminate the pollution produced in a manufacturing process. Instead of this "successful" temporary solution, an alternative solution that has been pursued is the implementation of waste minimization programs as part of an agenda towards a sustainable development.

Attempts have been made to promote the implementation of source reduction programs by identifying their potential benefits, including savings in waste management costs, reduction in the use of raw materials and energy supplies, and minimization of potential environmental liability. However, despite these and other benefits a report by the Environmental Protection Agency (EPA) (EPA, 1992) suggests that the majority of the US manufacturers have been slow to move away from the traditional end-of-the-pipe strategies. As this report suggests, the main reason has been the difficulty in establishing the various environmental costs associated with a particular operation.

The environmental costs should not be the only factor considered in the evaluation of source reduction alternatives. With the same degree of importance, the overall environmental impact of the process —generally difficult to quantify in monetary terms— should be considered as a complementary decision tool. Furthermore, as the investment question is analyzed under a broader perspective the analyst becomes aware of additional factors that the analyst or decision maker has no control over. Moreover, in most instances the decision to invest needs to be made with incomplete or uncertain information. Hence, one can question the applicability of the traditional deterministic approach used in the design or retrofit of industrial processes.

There are numerous procedures that have been proposed for the design and retrofit of chemical processes (Douglas, 1988; Douglas, 1995; El-Halwagi and Manousiouthakis, 1989; Fisher *et al.*, 1987; Fonyo *et al.*, 1994; Grossmann and Kravanja, 1995; Grossmann *et al.*, 1987; Gundersen, 1989; McNulty, 1994; Naka *et al.*, 1997; Pohjola *et al.*, 1994; Wilkdendorf *et al.*, 1998). However, only a few of them are aimed towards looking at alternatives that minimize the pollution generated within a process (Akehata, 1991; Alvaargaez *et al.*, 1998; Buxton *et al.*, 1997; CMA, 1993; Dantus and High, 1996; Douglas, 1992; Fonyo *et al.*, 1994; Hopper *et al.*, 1992; Mallick *et al.*, 1996; Manousiouthakis and Allen, 1995; Pennington *et al.*, 1997; Spriggs, 1994; Sudholter *et al.*, 1996). These methods generally look at options that are evaluated under a single objective approach, either minimize the amount of waste generated, where the objective function $z=f$(weight or volume); or maximize profit, where $z=f(\$)$. Yet, no detail is given on how this profit should be evaluated in order to incorporate all waste related costs.

Some work has been done in simultaneously evaluating alternatives under the two previous criteria —maximize profit and minimize the amount of waste generated— (i.e., Chang and Hwang, 1996 and Ciric and Huchette, 1993). In their procedure the waste reduction options are evaluated based only on a deterministic approach and do not consider the type of waste that is generated. The type of waste as a function of its toxicity characteristic is addressed for example by the methodologies proposed by Cabezas *et al.* (1997), Khan and Abbasi (1997), Koller *et al.* (1999), Mallick *et al.* (1996), Stefanis and Pistikopoulos (1997), and Stefanis *et al.* (1997). These methodologies focus also on a deterministic perspective and the first two do not consider the process' economic impact. The deterministic caveat, on the other hand has been addressed for example by Chaudhuri and Diwekar (1996), Chaudhuri and Diwekar (1997), Grossmann and Sargent (1978), and Ierapetritou *et al.* (1996), but only as a single objective optimization problem.

In this context, the main objective of this work is to develop a comprehensive methodology that takes into account the uncertainties present when evaluating process alternatives that seek to reduce the waste generated in a chemical process. The methodology attempts to incorporate and consequently evaluate the use of stochastic and multiple objective optimization techniques, to select the best alternative that maximizes the profit —that is the alternative with the lowest operating and waste related costs— and minimizes the environmental impact of a specific process. The present work goes further in determining the possibility of using the sequential process simulator ASPEN PLUS™ (version 9.3-1) for this task.

In order to test the applicability of the proposed methodology, the process for the manufacture of methyl chloride through the thermal chlorination of methane is used as a case study. This process taken from AIChE (1966) and from previous work by Dantus and High (1996) was selected due to its environmental restrictions and limitations and for its potential for improvement.

The development of a comprehensive methodology required the combination of different approaches, concepts, and tools from various disciplines. Therefore, to aid the reader in better understanding this dissertation a diagram of the proposed methodology (see Figure 1.1) is used continuously as a road map throughout each of the chapters. As each block in Figure 1.1 is discussed in detail, relevant background information is given to understand the concepts being used and to place them within their respective field and when applicable within the field of chemical engineering. By following this approach, the reader might not feel overwhelmed with a "typical" comprehensive background section that would attempt to cover all the topics dealt in this dissertation. Yet, since the main purpose is to develop a pollution prevention framework a separate section is included to understand the relevance of applying waste minimization techniques.

In summary, the questions that the present work attempts to answer are: (1) how to correctly evaluate waste related costs and the environmental impact of a source reduction project, (2) how to combine stochastic optimization techniques with multiple objective optimization methods, and (3) how to incorporate these optimization tools with the sequential process simulator ASPEN PLUS™. To address these questions, this dissertation is divided in seven chapters (see Table 1.1).

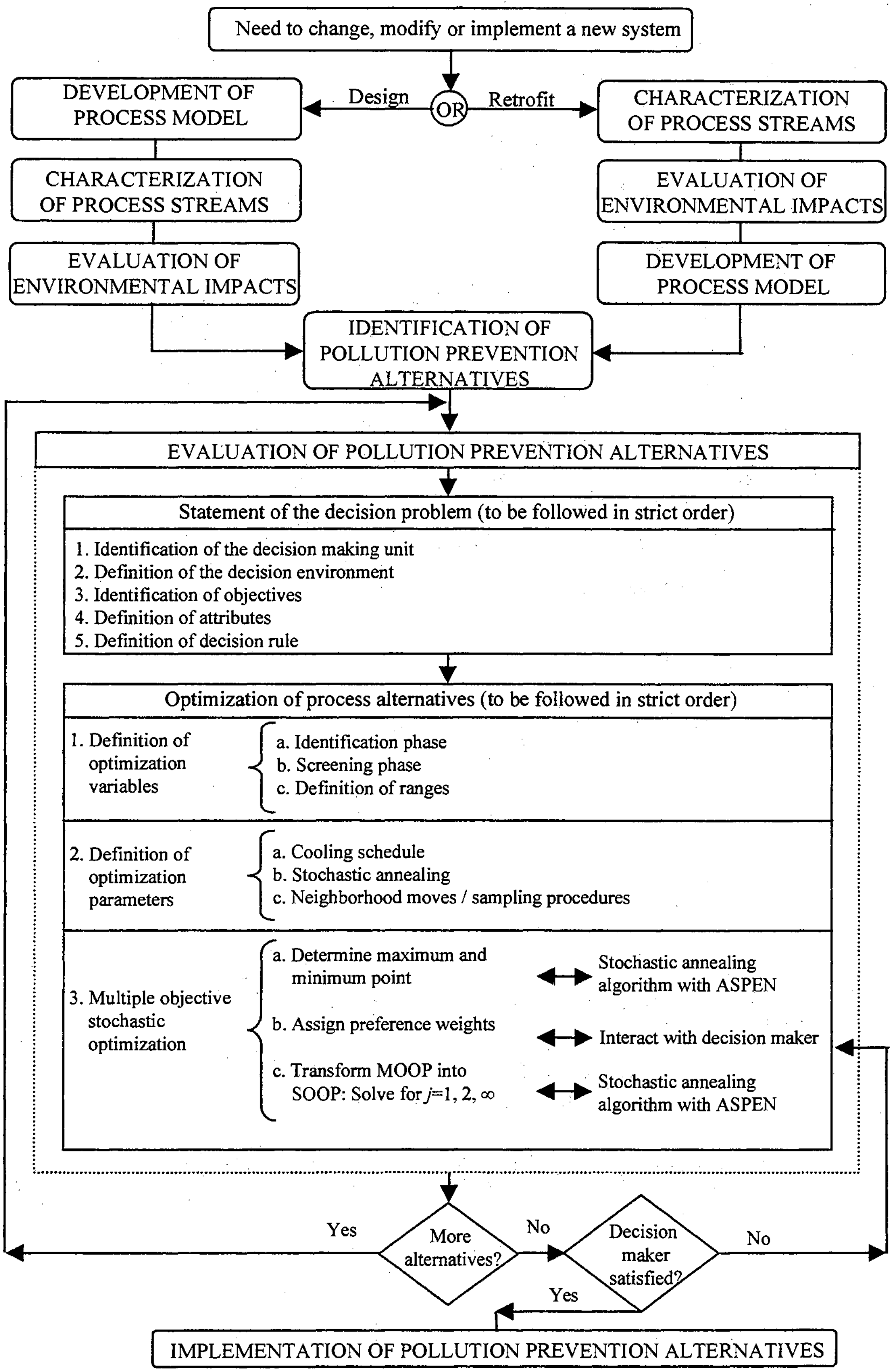

Figure 1.1: Outline of proposed methodology

Table 1.1: Description of contents

Chapter	Contents
2	Presents a quick overview of the waste problem, including some of the options that have been proposed to address it. This chapter expands the idea of waste minimization projects including the potential benefits that can be obtained from them. It serves to understand the importance and need to develop a waste minimization methodology.
3	Outlines the proposed methodology for implementing source reduction programs. It discusses the methodology's initial steps leaving the evaluation of process alternatives' step to be discussed in detail in the next four chapters.
4	Focuses on how the evaluation of investment options translates into a decision making problem. Here the discussion centers on the components used to define the decision problem, ranging from the individual(s) responsible for making the final decision to the criteria and decision rule used in the evaluation of waste reduction projects under uncertainty. As part of the decision problem's description, the chapter initially proposes evaluating alternatives only from an economic perspective. However, assigning a monetary value to environmental damage costs can be difficult or even unrealistic. Hence the process' cost evaluation is combined with an environmental efficiency that employs toxicological data to determine the operation's environmental impact.
5	Addresses the problem of measuring the process' profits by identifying the economic benefits of pollution prevention projects. It contains a detailed description of the various costs to be included in an investment comparison study, both from a traditional and environmental accounting perspective.
6	Discusses the optimization of process alternatives. It presents a review of optimization techniques for evaluating single and multiple objective optimization problems. After a brief review of discrete methods, the chapter focuses on the optimization of stochastic or random processes.
7	Continues with the discussion of optimization of process alternatives. It outlines the implementation of multiple objective stochastic optimization for the evaluation of waste minimization projects. It presents further, how this analysis can be made using the process simulator ASPEN PLUS™.
8	Uses the process for the production of methyl chloride through the thermal chlorination of methane to illustrate the application of the proposed methodology as described in Chapters 3, 4, 5, 6, and 7. Considering the various uncertainties related with the process, it suggests the best compromise solution for the continuous and binary variables evaluated.

CHAPTER 2

WASTE MINIMIZATION

The focus of this chapter is on the importance of developing a waste minimization methodology and the relevance of implementing source reduction programs. As can be seen in Figure 2.1, this chapter tries to answer the following question: What are the events that might trigger the need to change or modify an existing system or to implement a new one?

2.1 INTRODUCTION

Each year, the U.S. industry generates more than 14 billion tons of waste. This dramatic amount includes the gaseous emissions, solid wastes, sludge, and wastewater generated by the manufacturing, mining, and agricultural sector (DOE, 1997a). To manage these wastes, the most common approach has been to apply end-of-the-pipe treatment technologies which seek to eliminate as much as possible the amount of pollution produced. Even though it has been successful in achieving its goal, this approach can only be considered a temporary solution, since in the long run it is not very effective or economical. This is because in many instances the waste produced is only changed from one type of media to another. For example, a waste gas stream might be washed to remove its contaminants, changing the contaminants simply from the gas

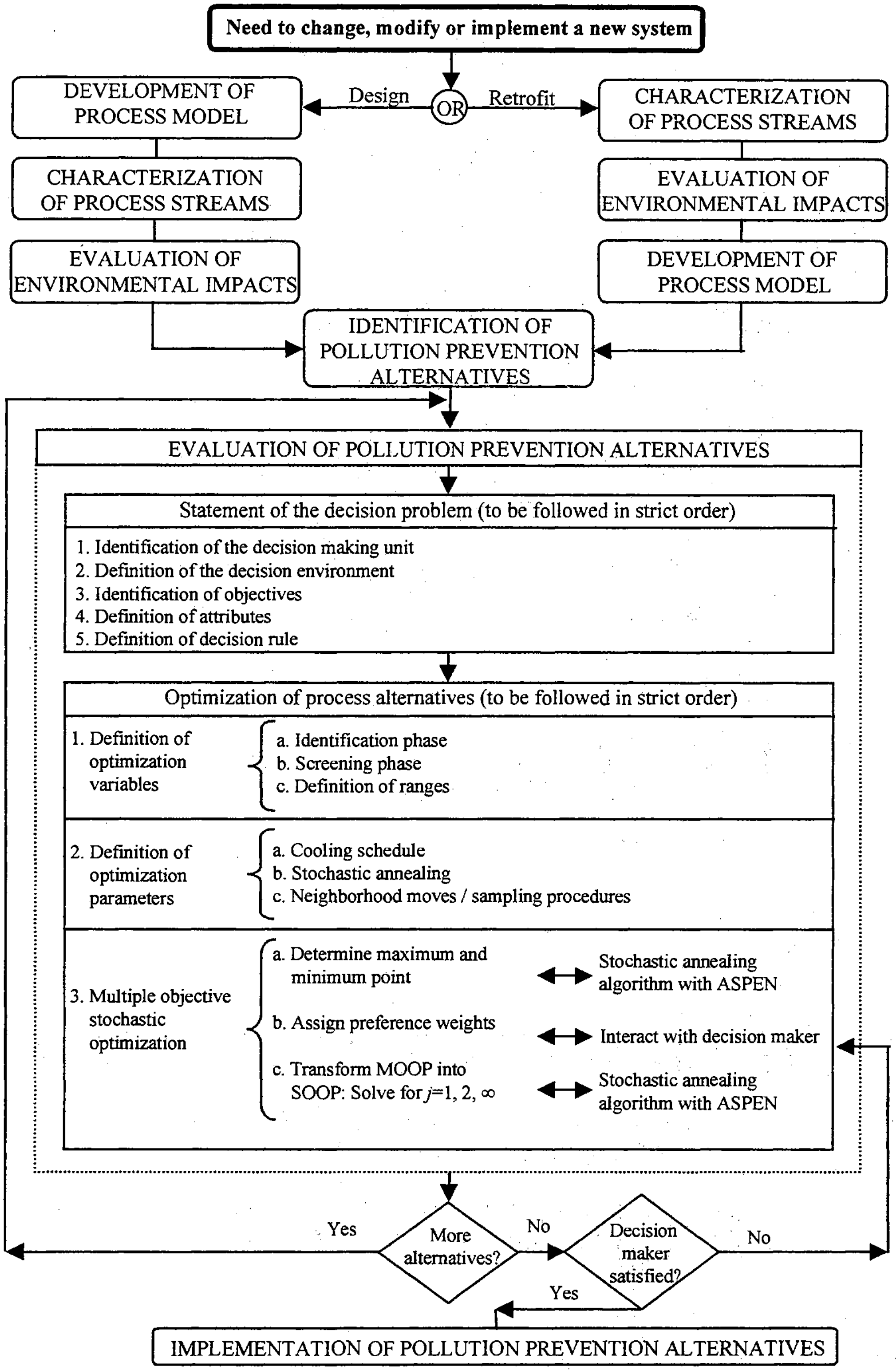

Figure 2.1: Road map[1] - Chapter 2

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[1] Lines/text in bold: topics discussed in this chapter. Shadow boxes: topics discussed in previous chapters.

stream to the liquid stream. In view of this, an alternative solution that is being pursued is the implementation of source reduction programs, or what is referred to as waste minimization programs where wastes are not created to begin with.

The present chapter after describing the waste problem discusses the benefits of applying waste minimization programs as a solution to this problem and as a part of an agenda towards a sustainable development. The chapter also analyses the implementation of source reduction activities from a regulatory and a voluntary approach. In summary, at the end of this chapter, the reader should be able to recognize the importance of implementing waste minimization programs.

2.2 DESCRIPTION OF THE WASTE PROBLEM

The waste problem has had a long history. However, not until 1962 when Rachel Carson published her influential book *Silent Spring* (Carson, 1962), did the general public become aware of the effects that chemicals such as DDT had on the environment. During this decade, the public concern and awareness started to increase and in December 1970, the United States Environmental Protection Agency (EPA) was created. Although prior to this date some environmental legislation had already been enacted such as the Clean Air Act (CAA) in 1955.

Within the international scenario, the first United Nations International Conference on the Human Environment held in Stockholm in 1972 raised a global environmental concern that has continued to increase. And in 1992, during the United Nations Conference on Environment and Development also known as the Rio Earth Summit, this preoccupation led to the establishment of international strategies for addressing specific environmental problems such as climate change and biological diversity. Furthermore, five years later, in 1997, a second conference on climate change held in Kyoto led to specific emission reduction goals. It should be pointed out that all these conferences have in general not led to the implementation of concrete global actions aimed at solving the environmental problem.[2] Nevertheless, these conferences have had positive impacts in the environmental agenda, particularly in the case of the industrialized world.

In the United States, the EPA has been evaluating since its creation the status of the environment so as to provide possible approaches and solutions to the environmental problem or what is to be referred to as the "waste problem". A measure that has been used to quantify this problem's magnitude is the Toxic Release Inventory (TRI). This requirement established under the Emergency Planning and Community Right to Know Act (EPCPRA) measures the United States progress' in reducing the amount of toxic chemicals that are released to the environment[3], including: (1) releases to air, surface water, and land; (2) underground injection; and (3) off-site transfers to treatment, land disposal, publicly owned treatment works (POTWs), recycling, and energy recovery facilities.

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[2] For example, in the case of Kyoto there was a big political turmoil before any agreements were reached. However, the last day of the conference several compromises were made and an agreement was obtained. Nevertheless, there are still several issues that need to be resolved in the future, including the enforcement mechanism and the role that third world countries should play in the environmental depletion problem. For an interesting review of these and other pending issues see Ott (1998).

[3] TRI release information by facility, industry type, and region is available through the Right-to-Know (RTK) Network that can be accessed on-line at http://www.rtk.net/www/data/tri_gen.html

According to TRI data (see Figure 2.2) there has been a significant reduction in the amount of chemicals released[4]. However, despite the reduction in the amount of chemicals released —almost 45% since 1988— there has been a small increase[5] in the amount of chemicals transferred to treatment, land disposal, POTWs, recycling, and energy recovery facilities; and a constant increase on the total amount of TRI chemicals in production related waste[6] (see Figures 2.3 and 2.4).

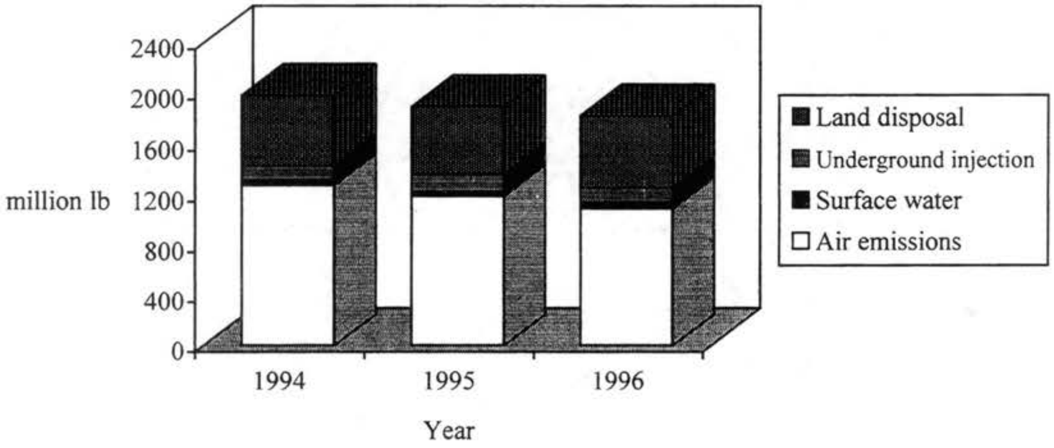

Figure 2.2: TRI total releases[7] (EPA, 1998)

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[4] A facility's reported releases may appear to diminish even without an actual reduction. For example, by taking advantage of a reporting exemption beginning in 1995, companies are exempt from TRI requirements if their total annual reportable amount for a specific chemical does not exceed 500 lb. Furthermore, since 1987 changes have been made to the list of chemicals to be included in the TRI reports. For example in 1995, 245 "new chemicals" were added that accounted for 237.7 million lbs. or 10.8% of all reported releases and 155.1 million lbs. or 4.4% of all transfers reported in that year (EPA, 1997a). Therefore, to compare release data on a yearly basis, the information presented in Figure 2.2 and subsequent TRI related figures correspond to a set of "core" chemicals that have remained unchanged.

[5] The increase is more evident if data for 1993 is included, as reported by EPA (1997a). However, this data is not given in Figure 2.3 since the 1994 and 1995 quantities given in EPA (1998) do not correspond to those reported a year earlier (EPA, 1997a). Hence Figure 2.3 only includes the data given by EPA (1998).

[6] The production related waste includes the quantity of TRI chemicals that are used for on and off-site energy recovery, the quantity recycled on and off-site, and the quantity treated on and off-site. In this manner, for example if 100,000 lb of benzene were combusted in an incinerator with a 99% destruction efficiency, the facility would report 99,000 lb as treated on-site and the remaining 1,000 lb would be reported as released

[7] Does not include delisted chemicals, chemicals added in 1995, ammonia, hydrochloric acid, and sulfuric acid. In addition, as of 1995, facilities are no longer required to report releases and transfers of non-aerosol forms of sulfuric and hydrochloric acid (EPA, 1997a). Release data is usually available after 18 months. That is, data for 1997 will be available approximately until June 1999.

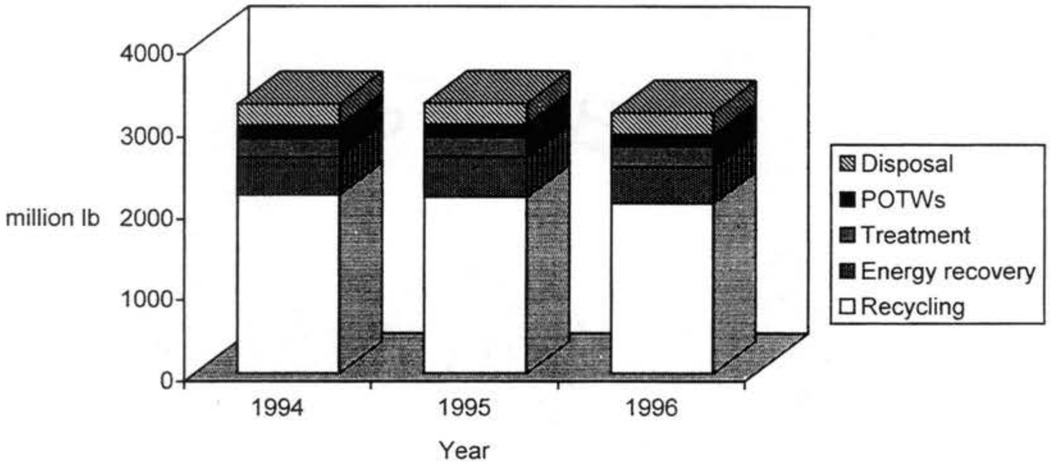

Figure 2.3: TRI total transfers (EPA, 1998)[8]

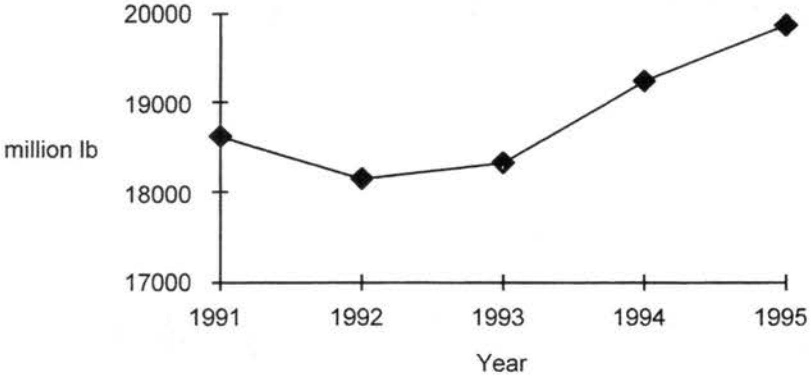

Figure 2.4: Quantities of TRI Chemicals in production related waste[9] (EPA, 1997a)

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[8] See footnote 7.

[9] The production related waste does not include the amounts related to one time events.

The waste problem is not only related to the amount of TRI chemicals released, but also to the quantity of waste generated, where waste is defined by the EPA as:

> anything produced by a process or by accident, which cannot be directly used onsite as a raw material for another process without some sort of treatment. A waste is also any material which cannot be reused onsite at all, and must be sent off for disposal or processing into another product or raw material. Chemicals which are off-specification, or become so due to age, are also wastes (Carlson, 1992, p. 95).

The U.S. industry, as was previously mentioned generates more than 14 billion tons of waste each year (DOE, 1997a). Most of this waste originates in the manufacturing sector of which 88% of non-hazardous pollution and over 95% of hazardous wastes[10] are generated in seven industries: aluminum, chemicals, forest products, glass, metalcasting, petroleum refining, and steel industries (DOE, 1997b)[11].

2.3 SOLUTIONS TO THE WASTE PROBLEM

The waste problem as presented in the previous section encompasses a broader range of topics than the ones described, such as economical, societal, international, and political factors. Defining a solution that seeks to resolve these issues is beyond the scope of this section. Nevertheless, the solutions to be discussed are concerned with reducing the environmental impact of a manufacturing process, for which there have been traditionally two approaches: the command-control and the use of economic instruments.

The command-and-control approach adopted by the EPA since its creation, has been the predominant strategy in pollution control and waste management. This approach

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[10] Hazardous wastes as defined in the Resource Conservation and Recovery Act (RCRA) exhibit one of four characteristics —ignitability, corrosivity, reactivity, and toxicity— or are considered as "listed wastes" based on their identification and production source.

[11] The amount of hazardous waste generated —as defined under RCRA— can be obtained from the Biennial Reporting System accessible through the RTK network (http://www.rtk.net/www/data/brs_gen.html). This system provides area, facility, and industry type information and represents the total amount of waste, not only the amount contained of a specific chemical, as is the case of the TRI reports.

has focused on reducing environmental degradation through a set of regulation and emission standards. Facilities that do not comply with these requirements are found in non-compliance, and subsequently are liable for a series of fines and penalties. The main advantage of this strategy is that it provides an approximate level of how much pollution will be reduced. In addition, it requires facilities to establish uniform abatement technologies; thus, protecting competition among them. However, as Bernstein (1993) suggests the command-and-control approach has been criticized for not achieving specific goals and deadlines, and for being economically inefficient and difficult to enforce. Furthermore, once the standards are achieved this approach provides little incentive for innovation in pollution control technology.

A second strategy for solving the pollution problem has been the use of several economic instruments that seek to promote cost-effective means for achieving acceptable levels of pollution. These tools include for example, effluent and emission charges based on the quantity and/or quality of pollutants discharged to the environment. Other similar charges include: tax differentiation to promote consumption of environmentally safe products, user charges such as fees to allow discharges of industrial wastes into public sewers, product charges added to the price of products or raw materials, and administrative charges such as permit or registration fees (Bernstein, 1993). All these instruments either directly or indirectly assign a penalty to the pollution generated in a facility. However, if these charges are not set correctly, some polluters may still choose to pollute.

In theory, economic instruments eliminate the need for regulations and enforcement activities. In practice though, they are usually combined with direct regulations or what was referred to as the command-and-control approach. In any case, whether the approach taken is that of the command-and-control, an economic strategy, or a combination of both, it is clear that the purpose that is being pursued is that of reducing the pollution generated in a process; hence, reducing the amount of pollution released to the environment; and, thus eliminating the requirements under any of the possible strategies. In this manner, the message that is being transmitted to the manufacturing sector is the one expressed in the Pollution Prevention Act of 1990 which declared it to be the national policy of the United States that

> pollution should be prevented or reduced at the source whenever feasible, pollution that cannot be prevented should be recycled in an environmentally safe manner whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner (EPA, 1997b, p. 269).

Consequently, the waste management hierarchy as defined by the EPA ranks pollution prevention as a top priority; followed by recycling, waste separation and concentration, energy and material recovery, waste treatment, and waste disposal (Mizsey, 1994).

2.4 WASTE MINIMIZATION

As was discussed in the previous section, waste minimization is a feasible solution to the waste problem has been a top priority in the EPA waste management hierarchy. The waste minimization goal was first introduced as a national policy in the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) (Clearwater and Scanlon, 1991). According to the EPA, waste minimization is the

> reduction to the extent feasible of hazardous waste that is generated prior to treatment, storage or disposal. It is defined as any source reduction activity that results in either (1) reduction of total volume of hazardous wastes; (2) reduction of toxicity of hazardous wastes; or (3) both, as long as that reduction is consistent with the general goal of minimizing present and future threats to human health and the environment (EPA, 1988).

Within this context, waste minimization incorporates two separate strategies (see Figure 2.5): source reduction and recycling. Source reduction, that includes product changes and source control, has been the goal pursued as the main road for pollution prevention. In 1996, as part of the TRI requirements, a total of 5,899 facilities accounting for 27.3% of all the TRI facilities, reported some kind of source reduction activities, of which good operating practices was the most frequent reported one (EPA, 1998). The remaining source reduction activities in decreasing order were: process modifications, raw material modifications, spill and leak prevention, cleaning and degreasing, surface preparation/finishing, inventory control, and product modification.

The recycling of wastes, the second waste minimization strategy, has seen a constant increase in the amount recycled both on-site and off-site since 1992 (see Figure 2.6). However, under some regulatory schemes simply reducing the volume of waste without a reduction of toxicity will not be considered waste minimization (LaGrega *et al.*, 1994). Moreover, when dealing with recycling what is being pursued is to reduce emissions not to increase the amount being recycled. This waste recycling increase can be considered as the main reason for which the quantities of TRI chemicals in production related waste have been incremented during the same period as was shown in Figure 2.4.

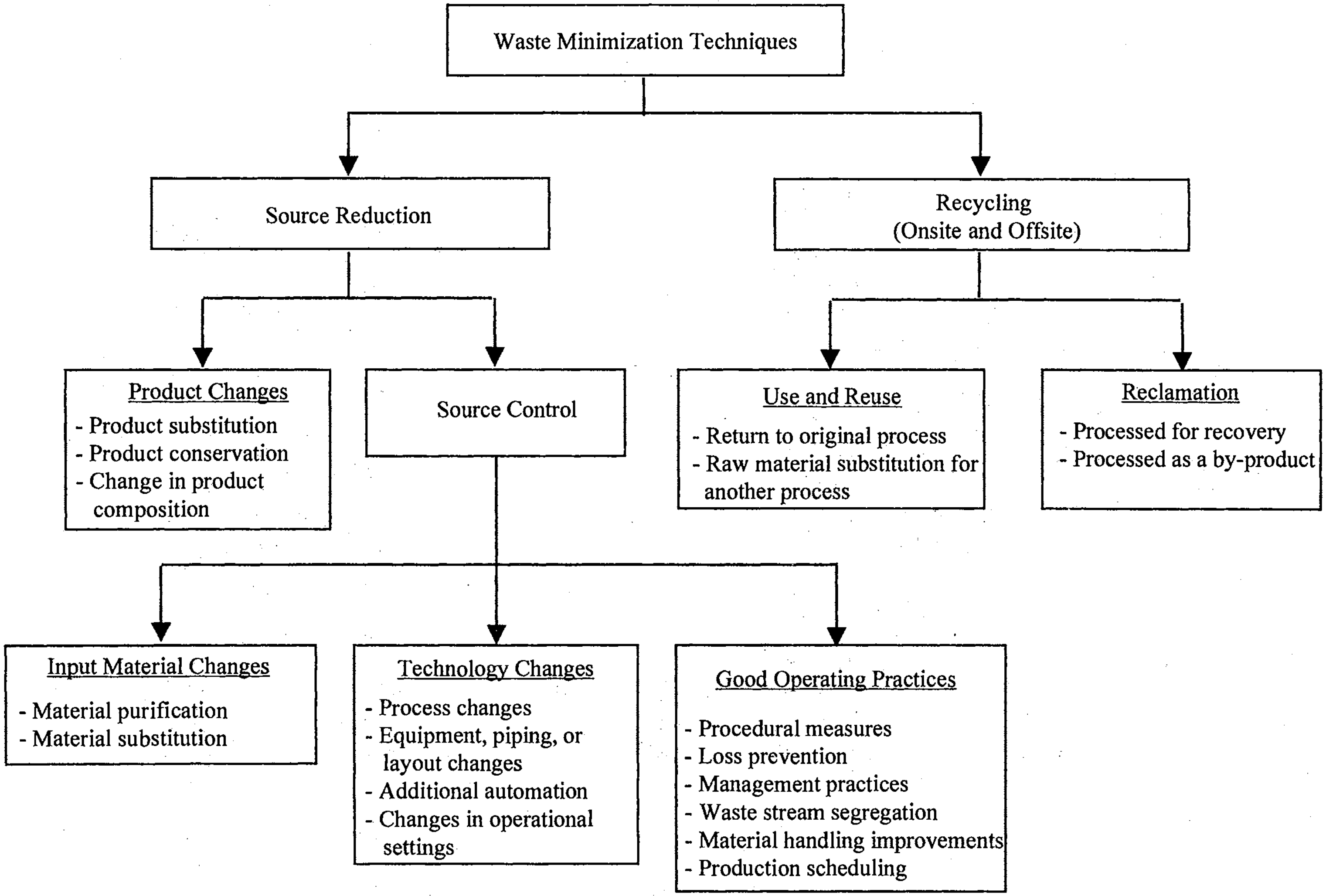

Figure 2.5: Waste Minimization Techniques (EPA, 1988; Theodore *et al.*, 1997)

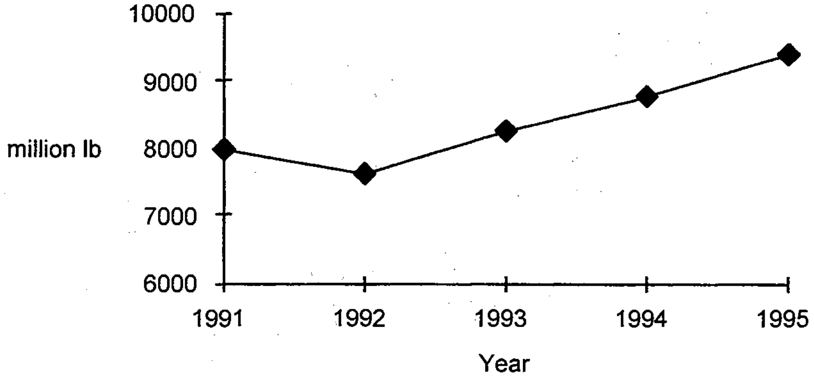

Figure 2.6: Quantities of TRI Chemicals in production related waste that are recycled on and off-site[12] (EPA, 1997a)

2.4.1 BENEFITS AND INCENTIVES OF WASTE MINIMIZATION PROGRAMS

Apart from protecting the environment and reducing the depletion of natural resources, the benefits and incentives to be obtained from applying waste minimization programs include a wide range of advantages to be obtained by companies that pursue such programs (see Table 2.1). In some instances, the potential benefits might be easy to identify and quantify. However in other cases, such as those listed under indirect benefits, the possible advantages might be very difficult to quantify, and even to identify. In addition, by participating in waste minimization programs companies may reduce their present regulatory requirements, as well as possible future regulations that might place a high economic burden on their operations. In any case, as is shown in Table 2.1 what is being pursued is to reduce costs and to enhance the corporate image.

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[12] The production related waste does not include the amounts related to one time events.

Table 2.1: Potential benefits of waste minimization (CMA, 1993)

DIRECT BENEFITS

- Reduced capital and operating costs for waste treatment facilities
- Reduced offsite treatment and disposal costs
- Reduced manufacturing costs due to improved yield
- Income or savings from sales or reuse of wastes
- Reduced environmental compliance costs (fines, shutdowns, etc.)
- Retained sales (processing that might have been shutdown because of poor environmental performance)
- Reduced or eliminated inventories and spills
- Reduced secondary emissions from waste treatment facilities

INDIRECT BENEFITS

- Reduced likelihood of future costs from: remediation, legal liabilities, and complying with future regulations
- Improved public health and community relations
- Increase environmental awareness by plant personnel and management
- Reduced societal costs

The main incentive for waste minimization programs has been their economic potential since EPA estimates that $120 billion is spent annually to treat or contain hazardous wastes once they are generated (Clearwater and Scanion, 1991). For example, in the case of the chemical industry, this sector from 1988 to 1993 averaged $5.6 billion in environmental outlays, that included operating costs and capital investments (McAllister, 1993). Moreover, these expenses have seen a substantial increase over the past years. For instance, by 1991 hazardous waste treatment and disposal costs had risen as much as 300% over the previous decade (Clearwater and Scanion, 1991).

2.4.2 SOURCE REDUCTION: A VOLUNTARY APPROACH

The potential benefits and incentives of waste minimization programs have led the industrial sector to look at these programs as a good manufacturing practice. Hence, the national policy expressed in the Pollution Prevention Act of 1990 is being followed not only through a regulatory perspective, but also through a voluntary approach.

As a result, the EPA has been developing and promoting voluntary partnerships as an alternative to the traditional command-and-control approach. The 33/50 program, the first major EPA voluntary pollution prevention reduction initiative, targets the reduction in direct environmental releases and offsite transfers of 17 high-priority TRI chemicals[13] by 33% in 1992 and 50% in 1995. This program originally established in 1991 has proven to be very successful. With the efforts of its 1,300 corporate participants, the

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[13] The 17 chemicals targeted by the 33/50 program are: benzene, cadmium and compounds, carbon tetrachloride, chloroform, chromium and compounds, cyanide compounds, methylene chloride, lead and compounds, mercury and compounds, methyl ethyl ketone, methyl isobutyl ketone, nickel and compounds, tetrachloroethylene, toluene, 1,1,1-trichloroethane, trichloroethylene, and xylenes.

33/50 surpassed its goal one year ahead of schedule, obtaining a 50.4% reduction in 1994 (EPA, 1996a); and by the year 1995, a 55.6% reduction was achieved (EPA, 1997a).

Several other partnerships have been established with the purpose of challenging businesses to prevent pollution (e.g., EPA's Green Chemistry Program). A detailed description of 28 such programs is given by EPA (1996b). Consequently, in 1995, over 6,000 participants involved in Partners for the Environment programs have saved $435 million while helping to cut toxic pollution, reduce solid waste, and lower greenhouse gas emissions (EPA, 1997b).

The voluntary approach does not only consider EPA-industry partnerships. Other programs that have emerged include the Chemical Manufacturing Association's Responsible Care program. Under this initiative —formally adopted in 1988—, the chemical industry commits itself to improving through tangible actions its performance in health, safety, and environmental protection (CMA, 1992). As part of this program, the chemical industry embraces the goal of long term reductions both in the amount of wastes generated and in the amount of compounds released to the environment. Other similar initiatives include the American Petroleum Institute's Strategies for Today's Environmental Partnership (STEP), the American Institute for Pollution Prevention (AIPP), and the Northeast Business Environmental Network (NBEN) (EPA, 1997b).

A recent initiative that is being designed for all industries worldwide is the International Organization for Standardization (ISO) 14000 standard series[14]. Their aim is to help organizations manage and evaluate the environmental aspects of their

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[14] Some standards have been available since early 1996. However the complete series is expected to be completed until 1999.

operations. Companies to be certified under these standards need to (Zuckerman, 1997, p. 275):

- Create an environmental management system
- Show evidence that they are in compliance with relevant laws, meaning the regulations of countries where they do business.
- Show commitment to continuous improvement and pollution prevention (e.g., recycling, process changes, energy efficiency, use of environmentally sound materials).

The ISO 14000 standard series will certainly have important benefits as organizations all over the world will start implementing an environmental policy. However, one of the problems of this standard is that it does not consider how a company should dispose of wastes or how it should reengineer its process to become more environmentally efficient. Also, it does not specify particular environmental performance criteria or pollutant/effluent levels, but only requires compliance with the local environmental regulations. Therefore, as Lamprecht (1997) suggests, a certificate issued in one country will not be equivalent to one issued in a second country, unless both countries have similar environmental laws and enforcement capabilities. This could encourage organizations to relocate to countries where there is a lack of environmental regulations and a weak enforcement authority[15].

The voluntary programs discussed in this section represent only a few examples of several programs that have emerged, both on the national and international level. The adherence of industry to such programs helps to reduce environmental related costs, enhances the company's image, and might help reduce environmental reporting requirements.

2.4.3 INDUSTRIAL POLLUTION PREVENTION SUCCESS STORIES

There are numerous examples of waste minimization projects that have resulted in both reduction of waste generated and the saving of considerable amounts of money (Benforado and Ridlehoover, 1991; EPA, 1997b; Freeman *et al.*, 1992; Lamprecht, 1997; Morris and Robertson, 1993; Thayer, 1992; Woodman, 1989). For example in a survey conducted by the firm INFORM, 29 small and very large companies, identified from 1986 to 1992 a total of 181 pollution prevention initiatives, where half of them reduced targeted waste streams by 90% or more. In addition, two thirds of them were quick and easy to implement, one-fourth required no capital investment, and two thirds resulted in a payback of six months or less obtaining $21 million in total savings (Lamprecht, 1997)[16].

However, despite these benefits and those discussed in the previous sections, a report by the EPA (EPA 1992) suggests that the majority of US manufacturers have been slow to move away from traditional end-of-pipe strategies and slow to move towards pollution prevention practices. Two main reasons can be attributed to this behavior. As will be discussed in the next chapter, the first and probably the main reason lies in the difficulty to determine and account for the process' environmental costs. Whereas the second reason can be related to the capital rationing process. In this manner, pollution prevention projects compete against each other and against other possible investments for the limited amount of capital that is available to the particular plant or to the whole firm. Hence, while the waste minimization alternative might be economically and

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[15] For example, as stated by Lamprecht (1997), in 1994 a few American firms looking for lower cost-labor, less stringent environmental regulations, and other economic advantages, elected to move their plants to other offshore sites rather than to comply with local regulations.

[16] It is interesting to mention that despite these encouraging findings, the majority of the companies had not established programs that would make aggressive pollution prevention possible.

environmentally feasible, another project that has a better estimated performance either economical or environmental, or that responds better to the company's strategic goals might be selected[17].

2.5 THE NEXT STEP: SUSTAINABLE DEVELOPMENT

The approach that was initially taken to solve the waste problem was to apply pollution control techniques in order to remove the pollutants before they reached the environment. The next step taken was to apply source reduction tools to eliminate pollution at the source, thus reducing future cleanup problems. However, these approaches focused only on in-plant related activities. Therefore, the next logical step was for industry to look outside the plant considering the development of the product, from raw materials, production, and product uses, to its final disposal. This approach, also known as life cycle analysis, takes only into account environmental issues and does not consider other factors such as economics, renewable/non-renewable resources, and social and health concerns. Logically, the next step is to include these factors into what is called design for sustainability, that can be defined as a "decision-making procedure that aims at achieving maximum benefits with minimum use of resources, by integrating all economic, social, human, environmental, and ecological concerns" (EPA, 1997b:240).

The concept of sustainability or sustainable development was not very clearly used until the mid 1980s after the World Commission on Environment and Development,

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[17] A recent report by Boyd (1998) serves as an example where capital rationing played an important role in the fate of the pollution prevention project. In this publication, the author analyses the reason why Monsanto, Dow, and DuPont faced with a potential environmental project chose not to implement it. However, it should be specified that capital rationing was not the only reason why the specific projects were not considered.

better known as the Brundtland Commission tried to define it in the report *Our Common Future:* "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs." (WCED, 1987, p. 43).

The Brundtland Commission was a result of a global concern about environmental degradation, especially after the international attention was raised by D.H. Meadow who said that:

> If the present growth trends in world population, industrialization, pollution, food production, and resource depletion continue unchanged, the limits to growth on this planet will be reached sometime within the next one hundred years. ...It is possible to alter this growth trends and to establish a condition of ecological and economic stability that is sustainable far into the future (Hammond, 1994, p. 187).

In this manner, the purpose of the Brundtland Commission was to "look into the alarming rate at which environmental resources were being consumed, at the level of their wastes, particularly in the cause of development, and at the waste in which developing countries were falling further and further behind the industrialized world in the standard of living." (Middleton *et al.*, 1993, p. 16)

Since it was introduced, the concept of "sustainable development" has been embraced by several multilateral institutions, and it is considered nowadays as the best guide in the fight against environmental degradation. However, there is still debate on how sustainability is to be measured. For a review of different possible approaches to accomplish this, see Farrell and Hart (1998).

2.6 SUMMARY

This chapter presented an overview of the concept of waste minimization from its background to its benefits. In summary, the main ideas to be taken out of this chapter include:

- The understanding of the magnitude of the waste problem.
- The solution of the waste problem involves a wide variety of factors including economical, social, international, and political factors.
- For reducing the environmental impact of a manufacturing process, there have been traditionally two approaches: command and control and economic instruments. These approaches send the message of looking at the possibility of implementing pollution prevention projects.
- Waste minimization is considered a top priority for the EPA and it includes source reduction and recycling. However, under some regulatory schemes simply reducing the volume of waste without a reduction of toxicity will not be considered as waste minimization.
- The industrial sector can obtain a wide variety of benefits from applying source reduction programs, including reduction in operating and environmental costs, and reduction of present and future regulatory requirements (e.g. remediation, liability, and compensation costs)
- The potential benefits have led the industrial sector to implement source reduction projects from a regulatory and voluntary approach.

These ideas are helpful in understanding the importance of developing a waste minimization methodology and of looking at potential pollution prevention projects, translating —as was shown in Figure 2.1— into a need to change or modify an existing system or to implement a new one.

CHAPTER 3

IMPLEMENTING WASTE MINIMIZATION PROJECTS: A GENERAL METHODOLOGY

After having looked at the benefits of implementing waste minimization programs and discussing what might trigger the need to implement such programs, this chapter presents an overview of the proposed methodology for identifying, evaluating, and implementing source reduction projects. As can be seen in Figure 3.1, this chapter focuses on the methodology's six major steps, leaving the evaluation of process alternatives —the backbone of this work— to be discussed in detail in the next chapters.

3.1 INTRODUCTION

The implementation of waste minimization programs depending on the scope of the project can encompass a series of activities that can vary in complexity. They can be implemented during various phases of the process, from the design stage to the retrofit of existing operations. For the case of process design, pollution prevention concepts should be incorporated as early as possible during the research and development stage. In a similar manner, retrofit projects should consider waste minimization initiatives throughout their implementation.

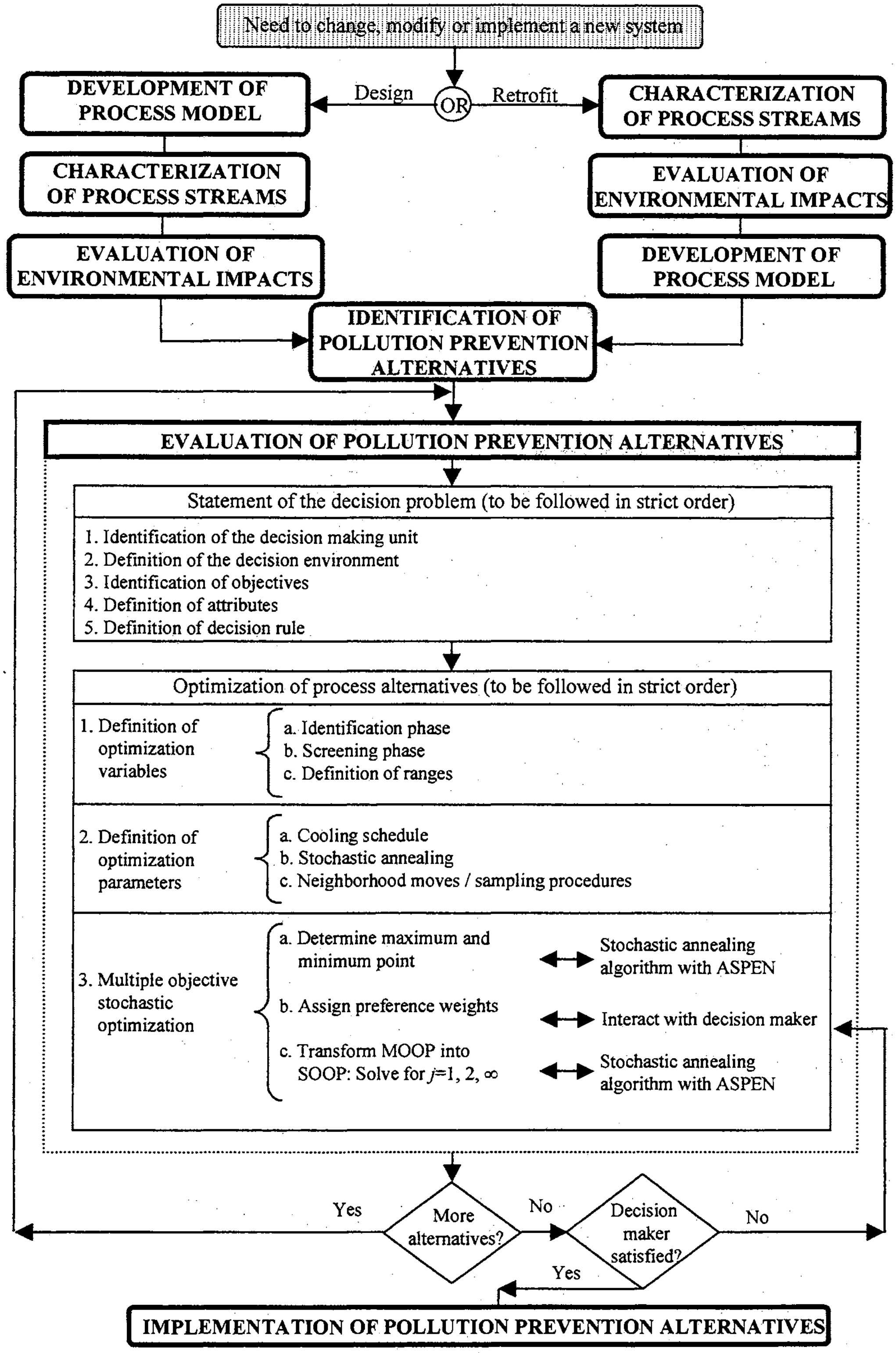

Figure 3.1: Road map[1] - Chapter 3

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[1] Lines/text in bold: topics discussed in this chapter. Shadow boxes: topics discussed in previous chapters.

In any case, whatever the scope of the project is, the proposed methodology to be applied in the implementation of waste minimization programs consists of six major steps[2] (see Figure 3.1): (1) characterization of process streams, (2) evaluation of environmental impacts, (3) development of process model, (4) identification of pollution prevention alternatives, (5) evaluation of pollution prevention alternatives, and (6) implementation of pollution prevention alternatives. As needed, this methodology is to be repeated until the specific goals and specifications have been met.

The six step procedure does not always need to be followed in the order presented. In some instances, as shown in Figure 3.1, when analyzing an existing process the characterization of process streams could be the initial step. However, initiating the procedure with the development of the process model might be more appropriate when designing a new system or when process data is not available.

3.2 CHARACTERIZATION OF PROCESS STREAMS

Process streams should be characterized by source, destination, flowrate, composition, and properties. As the CMA (1993) explains, the characterization study should not only include those streams classified as waste. Other process streams, such as feed and recycle, should be identified since they can affect the amount and type of waste that is generated, treated, or released to the environment. In this manner, a process stream

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[2] The basic idea behind the six step methodology can be traced back to the pollution prevention's basic framework proposed by the Chemical Manufacturers Association (CMA, 1993). Although there are some similarities with the CMA's five step methodology, especially in the first two steps, the proposed methodology expands these initial steps, includes an additional one —the development of the process model—, and redefines the last one. In addition, the proposed methodology presents a detailed description of how the identification and in particular the evaluation of pollution prevention alternatives should be performed; including, as will be described further, the effect of uncertainty in these two phases.

characterization table such as the example shown in Table 3.1, can be constructed. This table can serve as an initial tool to identify possible areas where it could be worthwhile to conduct source reduction studies.

The number of streams included in the characterization study depends on the complexity and scope of the waste minimization project. In some instances, characterization of every process stream might not be practical or even necessary. Furthermore, the level of detail of the characterization of the specific streams might not be the same for each one of them. Therefore, since the characterization study might involve some capital investment, a decision needs to be made as to which streams to include and to what degree of detail should the characterization study be undertaken. Using the information generated in the next step, a possibility is to include those streams that represent a potential environmental impact, a possible target of environmental regulations, and/or an important cost effect.

3.3 EVALUATION OF ENVIRONMENTAL IMPACTS

The information generated during the characterization process of the previous step, is used to identify the potential environmental impact of the different streams incurred from the possible release to air, water, and land. To accomplish this, the chemical components of each stream should be checked against the list of regulated chemicals that are considered to be potentially hazardous to the environment or to the human health[3]. In addition, components need to be identified if they are to be classified

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[3] The regulatory status of the chemicals can be obtained from several chemical lists that are associated with major environmental regulations. An alternative choice is to use the Stanford's University Chemical Safety Database. This database available on-line at http://www-portfolio.stanford.edu/100369, provides the

Table 3.1: Excerpts from the methyl chloride's process stream characterization table

Type	Stream ID	Source	Destination	State	Quantity (kg/hr)	Composition w%	
Feed	CH4	-	MX1	Vapor	2,386	CH_4	0.98
						N_2	0.02
Intermediate	3	CSTR	HX2	Vapor	19,187	CH_4	0.31
						HCl	0.27
						CH_3Cl	0.22
						CH_2Cl_2	0.11
						N_2	0.04
						$CHCl_3$	0.04
						CCl_4	0.01
						Cl_2	0.01
Waste	W2	ABS	-	Liquid	18,746	H_2O	0.72
						HCl	0.27
						CH_3Cl	≈ 0.0
						CH_2Cl_2	≈ 0.0
						N_2	≈ 0.0

as hazardous or if they exhibit properties such as ignitability, corrosivity, toxicity, reactivity, tendency for the material to decompose, and tendency to accumulate or concentrate in organisms. Furthermore, if the waste generated is to be treated or recycled, the environmental impacts of the treatment and disposal options should also be considered.

What might be helpful at this point is to combine the environmental impact information and the results obtained from the characterization of process streams to

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hazards and regulatory status of a large number of chemical components. Other alternatives include reference books that compile regulatory information for hazardous chemicals; for example see Pohanish (1997) and Theodore and Beim (1997).

construct Specific Chemical Flowsheets[4] (SFC) to identify the path taken by a critical component. For example, in the manufacture of methyl chloride the SFC for carbon tetrachloride is given in Figure 3.2. In this manner, pollution prevention alternatives that seek to reduce the amount of carbon tetrachloride generated might be easier to identify. Under the SCF approach, a stream is considered to be part of a path if the concentration of the chemical is greater than a reference concentration. The appropriate reference value will be a function of the chemical in question, its environmental impact, its economic importance, and the degree of recovery desired.

3.4 DEVELOPMENT OF PROCESS MODEL

The information generated in the previous steps is used to develop a process model that will serve as an analysis tool to evaluate the current performance of the

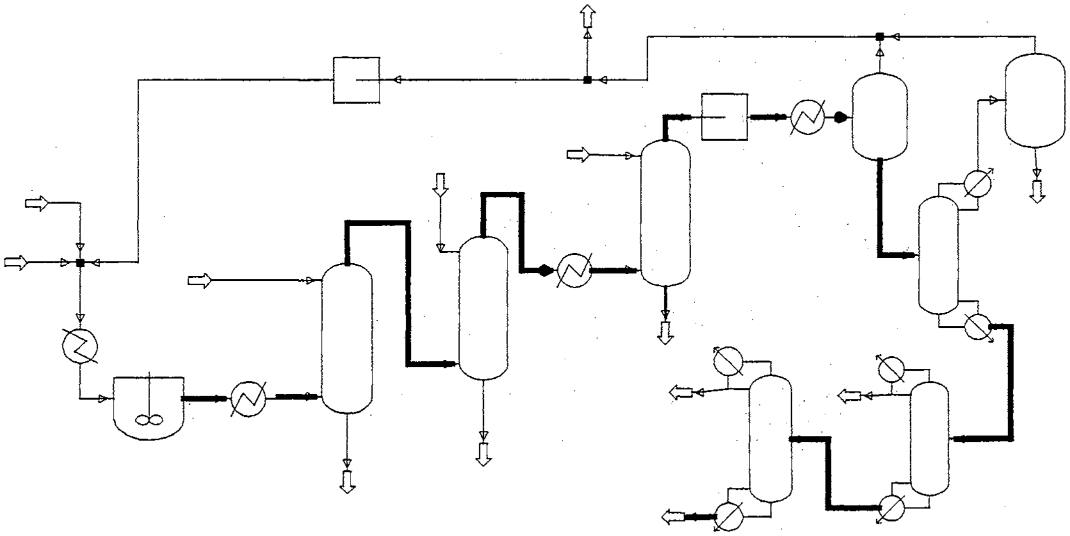

Figure 3.2: Carbon tetrachloride SFC for the methyl chloride process

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[4] The concept of Specific Chemical Flowsheets was developed from the idea given by Alliet Gaubert and Joulia (1997).

process —what is to be referred to as the base case process—, as well as an inexpensive experimental tool to evaluate the behavior of possible source reduction alternatives. An important factor in the development of the process model is to determine its scope by identifying the units and operations to be included. The more units or streams considered will make the model more accurate but will also make it more computationally intensive. Therefore, the units/streams to be included should be those that represent a potential environmental impact, a possible target for environmental regulations, and/or an important cost effect (as considered in previous phases).

In developing a process model, two approaches are possible: a theoretical and an empirical one. A theoretical model is used when the phenomena governing the process is well established and it is possible to develop a model based on theoretical considerations. These models are generally built with the aid of process simulators such as ASPEN PLUS™, HYSIM™, SPEEDUP™, and PROII™. These have proven to be successful in simulating chemical processes (Grinthal, 1993a).

On the other hand, the empirical model is useful when the process mechanisms are not well known, when it is too complicated to develop a model based on a theoretical approach, or when only an approximate response is desired. An empirical model can be developed from process data using techniques such as design of experiments (Box *et al.*, 1978) or using specialized process analysis software such as Process Insights®. Whichever model is developed, an empirical, a theoretical, or a combination of both, as Schad (1998) states a model does not guarantee a technically realizable process, and a model is only as good as the input fed to it.

3.5 IDENTIFICATION OF POLLUTION PREVENTION ALTERNATIVES

The previous steps combined with the process SCFs are used to identify pollution prevention alternatives to evaluate in order to determine the feasible ones to implement. This is generally accomplished with the use of hierarchical review approaches and other methods of structured thinking. These methods are based on decomposing the problem into smaller problems, and then finding their solutions in a structured and organized manner (Spriggs, 1994). These techniques are useful in generating and identifying possible alternatives. However, they are considered only as a screening tool and they do not attempt to find the best option.

In the structured thinking approach, one of the most important contributions is that of Douglas (1985), in which the design problem is reduced to a hierarchy of decisions consisting of five levels (see Table 3.2). Douglas' methodology, that has been successfully applied both for the design and retrofit of chemical processes, has had several modifications made including a more detailed synthesis of separation systems (Douglas, 1995).

The Douglas' procedure employs at each level a series of heuristic rules that can be used to identify pollution prevention alternatives. Several other techniques that have emerged can be used together with this procedure as a mean to generate additional alternatives. In particular, two important strategies that have been used for the separation system structure and the heat integration levels, are those of mass exchanger network (MEN) analysis (El-Halwagi and Manousiouthakis, 1989) and heat exchanger network

Table 3.2: Hierarchical decision procedure (Douglas, 1992)

Level 1: Input data

Level 2: Input – output structure of flowsheet

- Raw material purification
- Recycle and purge streams
- Recovery of byproducts

Level 3: Recycle structure

- Reactor systems
- Recycle streams

Level 4: Separation system

- Vapor recovery system (and gas separations)
- Solid recovery system (and solid separations)
- Liquid recovery systems
- Combine the separation systems for multiple plants

Level 5: Energy integration

(HEN) analysis (Linnhoff, 1994) respectively[5]. In addition, several lists have been published that can serve as complementary sources for source reduction ideas (see Table 3.3). All of these methodologies, some of which were originally developed for new processes, can be applied for both the design of new processes and the retrofit of existing ones. However, in the latter the evaluation of retrofit projects is not only subject to

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[5] The analysis of heat exchanger networks also known as pinch technology originally emerged during the energy crisis for the efficient use of energy. The basic principle behind pinch technology, is to maximize the heat transfer between process streams and minimize the utility requirements. In a similar manner, the analysis of mass exchanger networks is a systematic procedure to reduce the amount of wastewater generated by maximizing the mass transfer between lean and rich streams.

Table 3.3: Sources for pollution prevention ideas

Source	Description
Chadha (1994)	Presents 100 pollution prevention strategies based on changes in engineering design (storage and handling systems, process equipment, process control and instrumentation, and recycle and recovery equipment), process chemistry and technology (raw materials and plant unit operations), operations (inventory management, housekeeping practices, operating practices, and cleaning procedures), and maintenance practices.
CMA (1993)	Presents pollution prevention ideas for: byproducts, coproducts, catalysts, intermediate products, process conditions/ configurations, product, raw materials, and waste streams.
	Presents pollution prevention options for equipment design and operation.
Doerr (1993)	Introduces pollution reduction methods that deal with material handling, chemical or process changes, and time-related issues.
Dyer and Mulholland (1998)	Presents a list of strategies for a better reactor design and operation. Including raw materials, reactions, reactor mixing, reactor cooling and heating, and catalysts.
Gessner (1998)	Presents a guide for replacing hazardous materials used in a process with less hazardous substitutes.
Nelson (1990)	Presents a list of practical pollution prevention ideas for: raw materials, reactors, heat exchangers, pumps, furnaces, distillation columns, piping, process control and miscellaneous.
NMEMND (1998a)	Presents pollution prevention ideas for oil and gas exploration and production, transportation, gas processing, and oil field services.
NMEMND (1998b)	Presents alternatives for reducing waste based on the type waste being produced.
Siegell (1996)	Presents options for controlling VOC fugitive emissions from valves, connectors, flanges, pump and compressor seals, pressure relief valves, and other piping components; as well as VOC emissions from tanks, wastewater treatment facilities, loading operations, and vents.

safety, maintenance, operability and controllability —as is the case of grassroot designs—. The retrofit projects also need to take into account that (Gundersen, 1989):

- The physical space, foundation, and geographical location of the plant put restrictions on the economic feasibility of the project. In some cases a change to be made becomes very difficult or sometimes impossible.
- The modification of existing equipment has some restrictions.
- For small projects the equipment modification or installation of new equipment needs to be done during periods when the plant is shut down (i.e., due to maintenance activities). If the retrofit project is implemented during normal production activities any production lost will affect the alternative's economic evaluation.

In summary, as was shown in Figure 2.5, there are four possible types of changes that can lead to pollution reduction in a chemical process: (1) product changes, (2) input material changes, (3) technology changes, and (4) good manufacturing practices. Of these four changes, good manufacturing practices and operational settings (included in the technology changes classification), can be generally considered to be easy to implement, are probably the least expensive, and give positive results in waste minimization studies. However, when source reduction alternatives or any type of process change is to be considered it should be analyzed from a macro perspective. This means one should look at its effect on the particular process, as well as on any other process that could be affected from such modification and consequently its impact on the whole company.[6]

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[6] For example, a waste reduction study might suggest the possibility of recycling a waste stream, thus eliminating the need for a particular waste treatment/abatement unit. Shutting down this unit might have an

3.6 EVALUATION OF POLLUTION PREVENTION ALTERNATIVES

Once the pollution prevention alternatives have been identified, the next step is to evaluate them in order to determine the feasible ones or the best ones to implement.[7] There are traditionally two mathematical approaches to accomplish this (Spriggs, 1994): analysis and synthesis. In the analysis group or what is referred to as "design by case study," an initial structure is created for grassroot designs and for the case of retrofit projects an initial structure based on the existing process is developed. This structure is further analyzed through process models or process simulators. As a next step, modifications are proposed —for example using methods of structured thinking— and applied to the model to see if the process changes result in the desired improvement. When this process is repeated several times, design by case study can be very effective. However, by using this approach there is no guarantee that the best design has been found.

On the other hand, the synthesis approach seeks to find the best structure for the process given the inputs, outputs, process objectives and process constraints. The approach most frequently used is to create a superstructure of all possible connections among the units. Subsequently, optimization techniques such as Mixed Integer Non Linear Programming MINLP (Grossmann, 1989) can be used to identify the best structure. However, MINLP problems are difficult to set up and solve, especially for the case of sequential process simulators or what are referred to as "black box simulators",

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impact on other streams or processes. This impact should be considered as part of the alternative's evaluation.

[7] It is important to mention, that this phase will depend upon the number of alternatives developed, and as their number increases so will the complexity of the evaluation phase.

such as ASPEN PLUS™ (Diwekar *et al.*, 1992). In addition, as Spriggs (1994) suggests, it is difficult to incorporate the engineer's insights, creativity, and preferences into the evaluation process. Furthermore, as with the analysis case, the flowsheet selected will only be the best one among the alternatives evaluated, and this again does not guarantee that the optimum option has been found.

These two mathematical approaches —analysis and synthesis— have been traditionally applied based on a deterministic perspective. That is, the output of the system can be predicted completely if its input and its initial state are known. Hence, for a particular state of the system, a given input always leads to the same output. Consequently, decisions regarding the implementation of process alternatives are made under complete certainty.

However, there exists a certain degree of uncertainty that needs to be considered when process alternatives are evaluated. For example, within a manufacturing process there are several types of uncertainty that can be present (Ierapetritou *et al.*, 1996): (1) model inherent uncertainty (i.e., kinetic constants, physical properties, and transfer coefficients), (2) process inherent uncertainty (i.e., flowrate and temperature variations, and stream quality fluctuations), (3) external uncertainty (i.e., feedstream availability, product demand, prices, and environmental conditions), and (4) discrete uncertainty (i.e., equipment availability or other random discrete events). In addition, in the case of waste minimization projects, the regulatory environment also becomes an important source of uncertainty.

In dealing with this uncertainty, process alternatives can be evaluated using stochastic programming techniques. In the case of a stochastic system —given its input and its initial state— it is possible to predict only the range within which the output will fall and the frequency with which various particular outputs will be obtained over many repetitions of the observation. Hence, it is impossible to predict the particular output of a single observation system (Maisel and Gnugnoli, 1972).

Within this context, the alternatives identified during the previous phase will be evaluated considering their uncertainties by using stochastic optimization techniques in order to find the best feasible option among those evaluated (the details of how this evaluation is done is discussed in the next four chapters). This optimization study considers the evaluation of continuous variables, discrete variables, and —continuous or discrete— uncertain parameters. The continuous variables denote process operating conditions changes (e.g., temperature, pressure and flowrate) and the discrete or binary variables denote the existence of a specific piece of equipment or of a particular scenario.

3.7 IMPLEMENTATION OF POLLUTION PREVENTION ALTERNATIVES

After and during the evaluation of pollution prevention alternatives the analyst might identify additional source reduction projects that are worthwile to analyze, thus generating an internal loop as was shown in Figure 3.1. In addition, the methodology considers the interaction between the analyst and the Decision Making Unit (DMU). The latter, as will be discussed in the next chapter, decides which if any of the alternatives is to be implemented. However, before the final decision is made, additional alternatives might emerge from this analyst-DMU interaction. Furthermore, this interaction might lead to an adjustment in the preference information used during the evaluation of alternatives phase.

Finally, once a feasible pollution prevention alternative has been evaluated and identified, the next step is to implement such alternative. During its implementation, it is important to document the real benefits or savings that have been obtained from the waste minimization project. This might be helpful in the future in order to evaluate other pollution prevention projects, and serve as a proof of the potential advantages of applying such programs. In this manner, a comprehensive source reduction policy might be easier to implement throughout the company.

3.8 SUMMARY

This chapter presented an overview of the proposed methodology for identifying, evaluating, and implementing source reduction projects. In summary, the main ideas to be taken out of this chapter include:

- The methodology initiates with a need to change or modify an existing system or to implement a new one (this need was discussed in Chapter 2).
- The methodology includes six main steps, the order of which may vary depending on the scope of the project (e.g., design or retrofit).
- The six main steps include the characterization of process streams, the evaluation of environmental impacts, the development of the process model, and the identification, evaluation, and implementation of process alternatives.

CHARACTERIZATION OF PROCESS STREAMS

- Process streams (including waste and non-waste streams) are characterized by source, destination, flowrate, composition and properties.

- The number of streams included and the level of detail of the characterization depends on the complexity and scope of the project. A suggestion is to include those streams that represent a potential environmental impact, a possible target of environmental regulations, and/or an important cost effect.

EVALUATION OF ENVIRONMENTAL IMPACTS

- Considers the identification of the potential environmental impact of process streams incurred from the possible release to air, water, and land, as well as the regulatory status of the various process chemicals.

DEVELOPMENT OF THE PROCESS MODEL

- The process model serves as an analysis tool to evaluate the performance of the current process, as well as an inexpensive experimental tool to examine the behavior of possible source reduction projects.
- An important factor is to determine the model's scope by identifying the units and operations to be included.
- The process model can be developed using a theoretical or empirical approach. In this work, the path taken is to develop a theoretical model with the aid of the process simulator ASPEN PLUS™.

IDENTIFICATION OF POLLUTION PREVENTION ALTERNATIVES

- This step is usually accomplished with the use of hierarchical review approaches. One of the most important contributions is that of Douglas (1985). Two additional strategies mentioned are the heat and mass exchanger network analysis. Several other strategies for generating pollution prevention ideas were summarized in Table 3.3.

EVALUATION OF POLLUTION PREVENTION ALTERNATIVES

- This step considers the evaluation of process alternatives to determine the best one to implement.
- The alternatives are evaluated considering their uncertainties using stochastic optimization techniques to find the best feasible option among those evaluated.

IMPLEMENTATION OF POLLUTION PREVENTION ALTERNATIVES

- The evaluation and implementation of pollution prevention alternatives considers the interaction between the analyst and the decision making unit.
- Once the feasible pollution prevention alternative has been evaluated and identified, the next step is to implement such alternative.

CHAPTER 4

STATEMENT OF THE DECISION MAKING PROBLEM

The previous chapter presented an overview of the proposed methodology's six main steps. Initiating with the detailed discussion of the evaluation of pollution prevention alternatives, this chapter, as can be seen in Figure 4.1, focuses on the statement of the decision problem. That is who makes the decision, which criteria to use and how to measure it, and how should the decision be made based on the amount of information available.

4.1 INTRODUCTION

The decision to implement a waste minimization project, as was explained in the previous chapters, depends upon the potential benefits that can be obtained from that alternative. Once the benefits are correctly identified, the responsibility of the project's implementation relies upon the decision making unit (DMU) who determines which if any of the alternatives is to be considered. When the DMU is faced with all the necessary information, the choice might be quite straightforward. However, when dealing with real scenarios this is not always the case; since the DMU is generally faced with various types of uncertainties, as well as other decisions that could impact this decision.

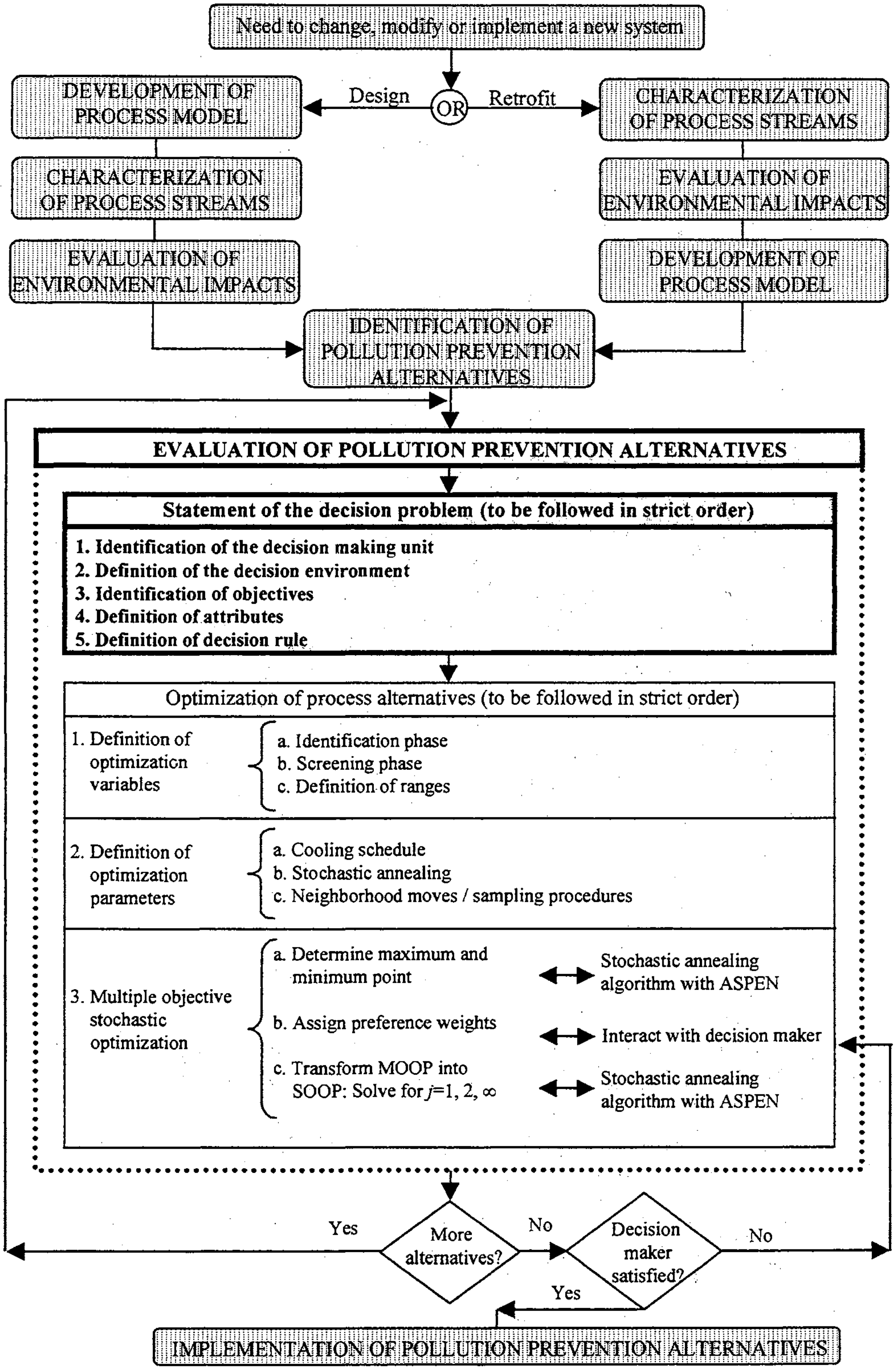

Figure 4.1: Road map[1] - Chapter 4

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[1] Lines/text in bold: topics discussed in this chapter. Shadow boxes: topics discussed in previous chapters.

In order to understand how the DMU makes the final decision, the analysis of source reduction alternatives can be undertaken from a decision theory perspective that has been applied in a wide variety of disciplines including engineering, economics, management science, and operations research (Anderson *et al.*, 1991; French, 1986; Goicoechea *et al.*, 1982; Hartmann, 1997; Holloway, 1979; Kirkwood, 1997; Kleindorfer *et al.*, 1993; Luce and Raiffa, 1957; Raiffa, 1968; Sengupta, 1982; Stermole and Stermole, 1990; Zimmermann, 1987). Decision theory has looked at the process through which an individual or group of individuals reach a decision, and through its understanding decision theorists have tried to either predict how these individuals will react on a particular issue or have looked at ways to help them make a better decision.

Under the framework of decision making, this chapter presents and discusses each of the five key components of the decision problem: the decision making unit, the decision situation, an objective or set of objectives, an attribute or set of attributes, and a decision rule (Chankong and Haimes, 1983). These components, as was shown in Figure 4.1, need to be specified before continuing on to the optimization of source reduction alternatives.

4.2 THE DECISION MAKING UNIT

The decision making unit or decision maker can be defined as the "individual or group of individuals who directly or indirectly furnishes the final value judgment that may be used to rank available alternatives, so that the ' best' choice can be identified" (Chankong and Haimes, 1983, p. 8). In this context a decision problem can be classified according to whether the decision is made by an individual or by a group of individuals having conflicting interests[2] (see Figure 4.2).

In the case of engineering and investment applications, the decision problem can usually be characterized as an individual decision making process in which a single person or an organization has a unitary interest motivating its decision. Therefore, considering that the decision to implement a pollution prevention project will be made by a single person, this work considers the analysis of waste minimization options as an individual decision making process.

4.3 THE DECISION SITUATION

Depending on the type and quality of the information or data available, decision problems can be classified whether they are made under conditions of certainty, risk, or uncertainty (Luce and Raiffa, 1957). Furthermore, as was shown in Figure 4.2, decisions can also take place under a combination of risk and uncertainty.

The decisions made under complete certainty consider that each action is known to lead to a specific output. That is, the output of the system can be predicted completely if its input and its initial state are known. Typically, when decisions are made under certainty an action is chosen to maximize or minimize a certain criteria.

Decisions made under risk —first studied in the analysis of gambling processes— apply to situations for when the outcomes of a process are not known with certainty, but about which good probability information exists or can be assumed. Hence, given the

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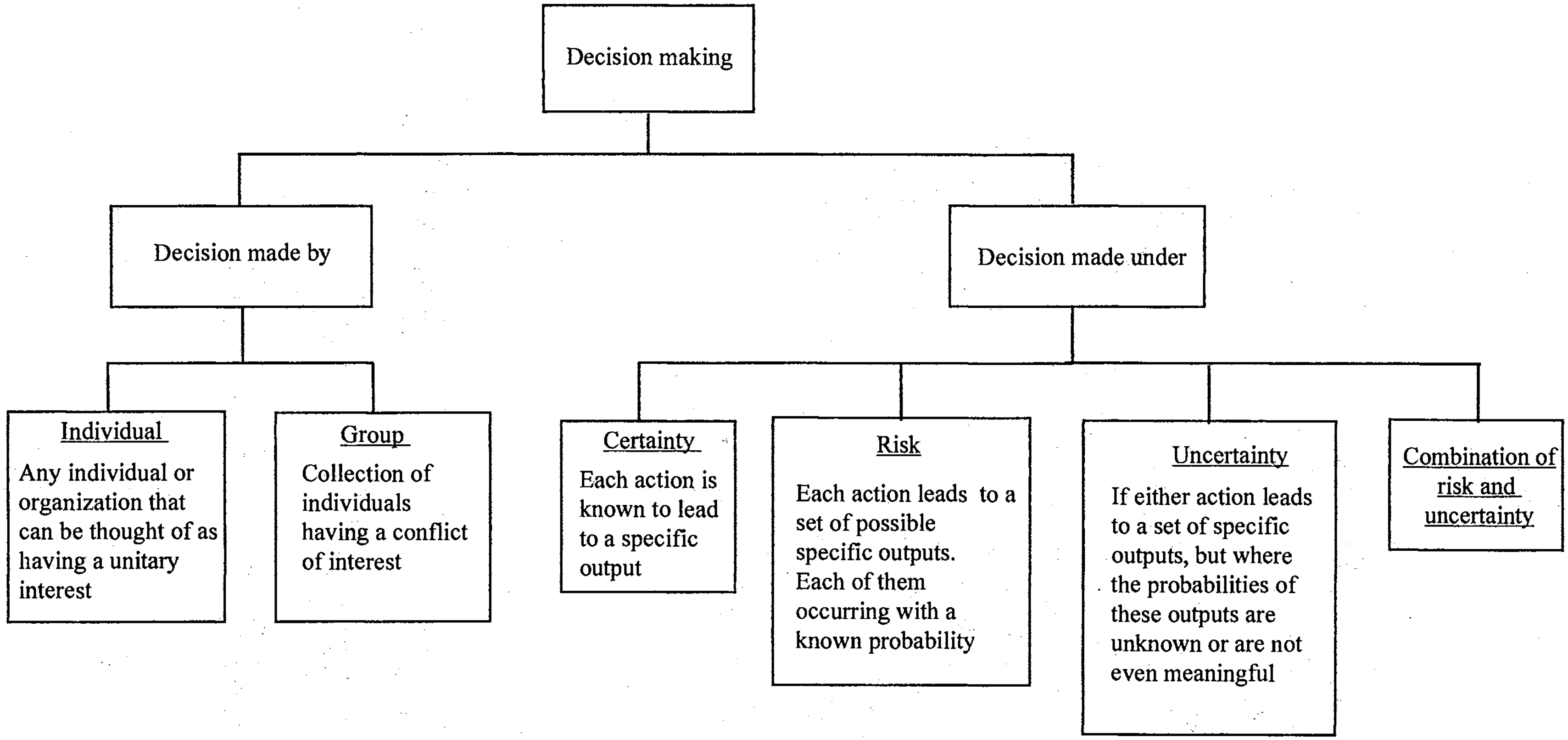
[2] Group decision making with conflicting interests, including the cases where the different parties may wish to cooperate to reduce the negative impact of a specific decision, is also known as "game theory". For a more comprehensive review on the subject see Kleindorfer *et al.* (1993) and Luce and Raiffa (1957)



Individual: Any individual or organization that can be thought of as having a unitary interest

Group: Collection of individuals having a conflict of interest

Certainty: Each action is known to lead to a specific output

Risk: Each action leads to a set of possible specific outputs. Each of them occurring with a known probability

Uncertainty: If either action leads to a set of specific outputs, but where the probabilities of these outputs are unknown or are not even meaningful

Figure 4.2: Decision making

system's input and initial state it is possible to predict only the range within which the output will fall and the frequency with which various particular outputs will be obtained.

The last realm of decision making processes encompasses the situation in which, as the previous case, the outcomes of a process are not known with certainty, but in this case there is not even good probability information. As Luce and Raiffa (1957) explain, in this situation it is assumed that the decision maker is "completely ignorant."

As can be expected, the complexity of the decision making process increases as the system's available information decreases. In theory, if the decision maker has sufficient knowledge, an uncertain scenario can be transformed to a risky one, and subsequently to one under complete certainty. However, in some instances obtaining such information, if at all possible, is time consuming and requires a certain amount of investment. Therefore, as Park and Sharp-Bette (1990) suggests, one needs to balance the value of reducing uncertainty with the cost of securing additional information. In addition, when dealing with investment decisions, the decision maker may choose to delay the investment, if by doing so some of the future uncertainties might be reduced. This "ability to delay an irreversible investment expenditure can profoundly affect the decision to invest" (Dixit and Pindyck, 1994:6). Furthermore, some uncertainties might only be resolved until the investment decision has been made and the project has started.[3]

As can be seen in Table 4.1, the uncertainty encountered in the evaluation of waste minimization alternatives, can include a broad range of factors. In general, when

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[3] At this point the irreversibility of a project, an important factor in investment decisions, should also be considered. This concept implies that an investment cannot be recovered, or at least not completely, once it is made. For a detailed description of this term and its effect on investment decisions see Dixit and Pindyck (1994).

Table 4.1: Uncertainty sources in analysis of waste minimization projects

Type	Example
Process model uncertainty	Kinetic constants, physical properties, and transfer coefficients
Process uncertainty	Flowrate and temperature variations, stream quality fluctuations
Economic model and environmental impact model uncertainty	Capital costs, manufacturing costs, direct costs, release factors, hazard values, hidden costs, liability costs, and less tangible costs
External uncertainty	Product demand, prices, feedstream availability, feed composition.
Discrete uncertainty	Equipment availability and other discrete random events.
Regulatory uncertainty	MACT standards, modified emission standards, and new environmental or safety regulations
Time uncertainty	Investment delays (i.e., the project might have a better performance in the future)

dealing with this uncertainty some amount of information is available or can be assumed. Therefore, in this work the evaluation of source reduction alternatives was made using methods suitable for making decisions under risk.

4.4 OBJECTIVES

The objective of a decision problem is a statement that represents the desired state of the system that the decision maker is trying to obtain. For example, typical objectives encountered in process design are "maximize profit," "minimize costs," or "maximize quality." Whatever the objective is, it represents the goal toward which the system should be going to and can be used as a performance measure to evaluate and compare process alternatives. It should be pointed out, that the objective expresses the ultimate goal and thus may or may not be achievable. There are decision problems for which one single objective might not be sufficient to describe the expected state of the system. In this case, one or more additional objectives need to be specified, thus generating what is called a multiple objective or multiple criteria decision making problem.

The analysis of pollution prevention alternatives has traditionally focused on the project's economic performance. That is, once the traditional and environmental costs associated with the particular operation have been identified, the alternative selected is the one that maximizes profit. However, the environmental costs should not be the only factor considered in the evaluation of source reduction alternatives. With the same degree of importance, the overall environmental impact of the process should be considered as a complementary decision tool.[4]

In general, these two criteria —profit and environmental impact— behave as competing objectives. This implies that a sacrifice in one of them is required to improve the performance of the second. These two competing objectives: "maximize profit" and "minimize environmental impact" are used in this work to evaluate pollution prevention alternatives. In this manner, the single objective decision problem is transformed into a multiple objective decision making scenario.

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[4] By way of illustration consider that two alternatives, A and B, are being evaluated. After a careful analysis it is determined that project A has a better economic performance yet it is expected to have a more severe environmental impact. So the question as to which alternative is better cannot be answered correctly unless both criteria have been considered.

4.5 ATTRIBUTES

Once the decision making unit (individual decision making process), the decision making scenario (decisions under risk), and a set of objectives ("maximize profit" and "minimize environmental impact") have been defined, an attribute or some measurable quantity is assigned to each objective to gauge its degree of achievement. The set of attributes is an important component of the decision problem, and its selection requires a careful analysis of the decision environment. In addition, as Chankong and Haimes (1983), state an attribute must satisfy two properties: comprehensiveness and measurability. An attribute is comprehensive if its value serves as a sufficient indicator of the degree to which the objective has been met. While, on the other hand, its value has to be reasonably easy or practical to measure.

The evaluation of waste minimization alternatives, as described previously, encompasses two objectives: "maximize profit" and "minimize environmental impact." The attribute assigned to each one of them is described in detail in the next subsections.

4.5.1 MEASURING THE PROFIT OF ALTERNATIVES

The first objective used to evaluate source reduction options seeks to maximize the profit that can be obtained from a particular investment. Different evaluation techniques have emerged to aid investors in measuring the profit to evaluate and compare alternative investments.

These economic comparison techniques can be divided in two major groups: those that include the time value of money (TVM) and those that do not include it. For the case of the TVM methods, their use can be traced back to as early as the 16th century.

However, it was not until the 1960s that these techniques were used as an investment appraisal tool generally accepted and applied in industry (Lefley, 1997).

Among the TVM methods used most are the Net Present Value (NPV) and the Internal Rate of Return (IRR). Despite their popularity, a controversy still exists between which method is the most appropriate and the most widely employed (Brealey and Myers 1988; Carroll and Newbould, 1986; Weaver, 1991; Woinsky, 1996). Lefley (1997) suggests that the IRR is still the method used most, while a survey published by Remer *et al.* (1993) reports a shift from the use of IRR to NPV. Whereas, the Environmental Protection Agency (EPA, 1995a) reports that the cash payback method (PB) is used more than the IRR and NPV methods.

To remove the controversy surrounding the selection of the best economic criterion to be used in this work, a comparison study was made between 19 economic tools[5] (see Table 4.2). This study included the analysis of 5 non-TVM and 14 TVM methods using 13 case studies that were taken from engineering and non-engineering sources (see Appendix A).

As can be seen in Appendix A, the choice of an appropriate attribute to measure the degree to which the objective of "maximizing profit" has been met, is not quite straight forward. It depends on the specific characteristics of the projects being evaluated

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[5] The methods evaluated represent only a small group of the economic analysis methods that have been proposed in the literature over the years. A recent performance measure that is worth mentionining is the Economic Value Added (EVA)™ method that has been gaining popularity in the corporate sector. The EVA developed by Stern Stewart & Co. (Stewart, 1991) measures whether or not value is being added to the company and "creatively links the firm's accounting data to its stock market performance" (Bacidore *et al.*, 1997:11). Since the firm's stock market performance is not to be considered at this point in the evaluation of waste reduction alternatives, the EVA, and other similar approaches, such as the refined economic value added (REVA) method and the cash flow return on investment evaluation model (Bacidore *et al.*, 1997; Ellott, 1997), are not included in the comparison study.

Table 4.2: Economic evaluation tools compared[6]

TVM Methods	Non - TVM Methods
Net present value	Cash payback method
Future worth	Payout period
Annual equivalent profit	Rate of return on investment
Net return rate	Average return on book value
Profitability index	Profit to investment ratio
Premium worth percentage	
Internal rate of return	
Overall return rate	
Discounted payback period	
Net payout fraction	
Payout period including interest	

and on the environment under which the decision is taken (certainty, risk, or uncertainty). However, based on the discussion given in Appendix A, the annual equivalent profit (AEP) will be the one used in this study[7]. The AEP can be considered as equivalent to the typical NPV approach. Yet in this case, the AEP is evaluated by multiplying the estimated NPV times an annuity factor A_f (see Equation 4.1)

$$AEP = NPV(A_f) = \left[\sum_{n=0}^{Ny} \frac{F_n}{(1+i_r)^n}\right]\left[\frac{i_r(1+i_r)^{Ny}}{(1+i_r)^{Ny}-1}\right] \qquad (4.1)$$

where:

i_r = interest rate

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[6] A brief description of each of the economic evaluation tools is included in the first part of Appendix A.

F = cash flow

n = number of years

Ny = project lifetime

The annuity factor facilitates the comparison of investment alternatives with different project lifetimes without the need —as is the case of the NPV— of replicating the various cash flows. This replication, also known as the chain rule, as explained in Appendix A has raised several concerns that might question the final ranking of alternatives. And since the lifetime of a project might not always be known with certainty, the use of the AEP criterion becomes a more appropriate choice[8].

The cash flow term in Equation 4.1 can be defined as the cash inflow minus the cash outflow, or as a function of the revenue obtained, the manufacturing costs, and the environmental costs (the details of how these costs are calculated are given in Chapter 5). In addition, depreciation charges, taxes, and inflation should also be considered[9]. Taking into account this information, the cash flow can be calculated in a tabular form (Park and Sharp-Bette, 1990; Peters and Timmerhaus, 1991) or with Equation 4.2.

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[7] It should be pointed out that when the information is presented to the decision maker other criteria such as the discounted payback period or the profitability index might be useful to include.

[8] In some instances, the use of the AEP method might not correctly identify the best option when dealing with different project lifetimes. As Ancel and Griffiths (1996) demonstrate, this ranking error can occur when a crossover point exists and its effect is not adequately considered in the investment evaluation. These authors further prove, that as long as the projects' rates of return ($i_{r,A}$ and $i_{r,B}$) are equal a crossover point does not exist. Unless the presence of this point is taken into account, this equality condition prevents the use of different discount rates as a measure of the projects' riskiness. However, in the present study, the discount rate will be used only as a financial indicator since, as will be discussed in the next section, the projects' riskiness is incorporated throughout the model evaluation. Therefore, the discount rate equality condition will be taken as valid throughout the analysis of waste reduction alternatives.

[9] When investment alternatives are evaluated, only additional costs that result from the alternative selected need to be included. For example, existing overhead costs such as salaries and administrative costs need to be paid regardless of the acceptance of the project.

$$F = (F_i - F_o) f_i (1 - Tx) + I_D f_D Tx \tag{4.2}$$

where:

F_i, F_o = Cash inflow, cash outflow

f_i = Inflation factor

I_D = Depreciable investment

Tx = Tax rate

f_D = Depreciation factor

The inflation factor in Equation 4.2 considers the annual inflation rate[10] (see Equation 4.3),

$$f_i = (1 + i_f)^n \tag{4.3}$$

where:

i_f = Annual inflation rate

that can become an important factor when evaluating investment alternatives. In particular, since its value can exhibit fluctuations during the project's lifetime. For example, in the United States, even though the annual inflation rate has seen small variations in the last few years; within the last 30 years, it has varied from 1.5 to 14% (Gaske, 1997).

The depreciation factor in Equation 4.2 considers the total depreciation cost of the investment, that is defined as the original value minus its value at the end of the depreciation period. These costs are prorated throughout the project's life and are included as part of the operating expenses, affecting the profits earned by the company and thus its income taxes. There are several methods that are used for estimating the project's depreciation charges, including: the straight line method, the declining balance method, the sum-of-the-years-digits method, the sinking fund method, and the Modified Accelerated Cost Recovery System (MACRS)[11]. As suggested by Peters and Timmerhaus (1991) the choice of the appropriate method depends on the type and function of the property involved and on the analysis of the existing circumstances[12]. However, whichever method is selected, the same one should be used throughout the evaluation of project alternatives, so as to maintain the same basis of comparison. In the present study, due to its simplicity, the method selected was the straight line depreciation; that can be applied individually, on a per item basis, or by grouping items with similar characteristics or lifetimes (see Equation 4.4).

$$I_D f_D = \frac{I_D - S_v}{Ny} \tag{4.4}$$

where:

S_v = Salvage value[13]

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[10] Inflation is defined as "a persistent rise in the prices of a Consumer Price Index type basket of goods, services and commodities that is not offset by increased productivity" (Stermole and Stermole, 1990, p. 199).

[11] The MACRS adopted as part of the Tax Reform Act of 1986 combines the use of the double declining balance method and a modified straight line depreciation.

[12] For a comparison of the different depreciation methods see Peters and Timmerhaus (1991, p. 291).

[13] The salvage value is defined as " the net amount of money obtainable from the sale of used property over and above any charges involved in the removal and sale" (Peters and Timmerhaus, 1991, p. 276).

Finally, before describing the second attribute for evaluating source reduction alternatives, one should be aware that the decision to invest should not be made only based on a quantitative analysis of the cash flows. If qualitative issues are not included as part of this analysis, the NPV, as well as the AEP, can be seen "more as a constraint than as a decision tool" (Shank, 1996, p. 196). For example, in a survey published by Carr and Tomkins (1996), the authors report on a shift from the use of discounted cash flow techniques[14] towards a more strategic approach. This approach referred to as Strategic Cost Management (SCM) involves the combination of three types of analysis, that should be included as part of any investment decision: the value change analysis, the cost driver analysis, and the competitive advantage analysis (Shank, 1996).

4.5.2 MEASURING THE ALTERNATIVES' ENVIRONMENTAL IMPACT

The damage costs incurred by a process include the costs to individuals, society, and environment. Even though, these costs might have an important impact in the waste characterization process, they represent one of the most difficult factors to evaluate. The difficult task of estimating these costs has been approached in several methods. Pearce and Turner (1990) argue that monetary values should be placed on the services provided by the environment. Peskin (1989) suggests that valuation methods should include the costs equal to the foregone benefits if the polluter were denied access to the environment.

Another possible approach is the use of performance standards, where the government imposes pollution or waste taxes on firms that do not meet these standards.

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[14] For example, in the automotive industry, *Nissan* deliberately avoids the use of NPV on major investment decisions (Carr and Ng, 1995).

This tax would give firms an incentive to produce relative little waste (Kunreuther and Patrick, 1991). In the same context, Hahn and Stavins (1989) suggest a marketable or tradable permit system for managing pollution. The idea is to specify through permits a certain level of waste. Firms whose waste was below specified levels could sell their permits or use them in other phases of their operation. Thus, encouraging firms to adopt new technologies for reducing waste below their permit level. However, several questions remained unanswered, including how to determine the waste level, how the toxicity of the waste should be taken into account, and how will the levels change with time as firms develop ways to manage their waste production. A review of the benefits and disadvantages of these and similar approaches is given by Bernstein (1993).

The previous methods, as well as others proposed, do not specifically address how are the damage costs to be evaluated and accounted for. Consequently, other authors such as Powell (1996) suggest the use of non-monetary evaluation techniques. In this case, the damage costs of several process alternatives are evaluated using a multicriteria evaluation method that incorporates the use of weighing factors to be defined by the decision maker. However, these factors might not be easy to identify and will vary according to the decision maker.

The complexity associated with damage costs identification can be caused by the fact, that these costs specific to each chemical and process can be considered not to be in control of the industry's hands. That is, once the release leaves the facility it is difficult to control and/or quantify its fate and effect on the environment. Hence, there is a high level of uncertainty associated with such determination.

Starting from the work by Mallick *et al.* (1996), the approach suggested in this work to account for the damage costs consists in the use of a non-monetary valuation technique that calculates the environmental impact of each chemical present in a waste stream, in terms of Environmental Impact Units (EIU) per kilogram of product produced (see Equation 4.5).

$$\theta = \frac{\sum_{i=1}^{n}\sum_{j=1}^{m} w_i m_{j,i} \Phi_j}{P} \tag{4.5}$$

where:

θ = environmental impact (EIU/kg)
w_i = Flowrate of waste stream *i* (kg/hr)
$m_{j,i}$ = Mass fraction of component *j* in waste stream *i*
Φ = environmental impact index of chemical *j* (EIU/kg)
P = product flowrate (kg/hr)

The incorporation in Equation 4.5 of the product obtained, allows to estimate the environmental impact of the process per unit mass of product produced. This "environmental efficiency" is an important factor to consider when comparing source reduction alternatives. Since the "waste streams" might not be the only emission source in the process, a question arises weather Equation 4.5 should include only the environmental efficiency of these "streams". As Siegell (1996) suggests, based on studies in the United States, the largest source of VOCs released —accounting for 40 to 60%—, is that of fugitive emissions from piping and other fluid handling operations. In addition, VOCs fugitive emissions can also come from storage tanks, loading operations, and wastewater treatment units. Subsequently, if these emissions, as well as other possible accidental releases are not taken into account, the environmental impact of the process might not be correctly evaluated. In this context, a factor that accounts for the release potential of a particular stream —including waste and non-waste streams— is incorporated into Equation 4.5 (see Equation 4.6).

$$\theta = \frac{\left\{\begin{matrix}\text{release}\\ \text{factor}\end{matrix}\right\}\left\{\begin{matrix}\text{flowrate}\\ \end{matrix}\right\}\left\{\begin{matrix}\text{mass}\\ \text{fraction}\end{matrix}\right\}\left\{\begin{matrix}\text{environmental}\\ \text{impact index}\end{matrix}\right\}}{\left\{\begin{matrix}\text{product}\\ \text{flowrate}\end{matrix}\right\}} = \frac{\sum_{i=1}^{n}\sum_{j=1}^{m} r_i f_i m_{j,i}\Phi_j}{P} \tag{4.6}$$

where:

r = release factor

f = flowrate (kg/hr)

The release factor in Equation 4.6 can take values from 0 to 1, depending on the particular process stream. For the case of waste streams, r=1, whereas for non-waste streams, $0 \leq r \leq 1$. Estimating the release factor is equivalent to calculating the probability of obtaining a release from a specific stream. This usually can be done considering past data and experiences related to the process under study. Based on the categories presented by Kolluru (1995), a guideline for estimating r based on the expected frequency of the release is given in Table 4.3.

In order to evaluate the environmental impact index, several methods have been proposed for scoring or weighting chemicals based on potential toxicity and/or exposure. A review of sixteen such methods that employ qualitative, ordinal,

Table 4.3: Guidelines for estimating the release factor

Frequency	*r*
Constant: Stream characterized as waste stream	1
Frequent: Release expected to occur several times a year	0.3 - 1.0
Occasional: Release expected to occur several times during the facility lifetime	0.1 - 0.3
Remote: Release expected to occur about once during the facility lifetime	0.01 - 0.1
Not expected: Release highly unlikely to occur during the facility lifetime	< 0.01

proportional, or calculated weights is presented by Bouwes and Hassur (1997a)[15]. Based on this analysis, Bouwes and Hassur (1997a) present an alternative method to rank the chemicals included as part of the TRI reporting requirements. Their method is a site specific technique that evaluates the toxicity of a chemical based on its carcinogenic and non-carcinogenic effects. Once a toxicity weight is assigned, the method considers the fate of the pollutant on the environment through several dispersion models that account for weather, geographical, and physical characteristics of the industrial site under evaluation. This information is combined with the size of the potentially exposed population to calculate a chronic human health indicator that can be used as a measure to

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[15] Most of the methods reviewed were developed by the EPA. However, not all of them have been officially published or evaluated.

compare the TRI data reported. A draft is also presented for estimating a TRI chronic ecological indicator. However, no data or details are given for this ecological indicator.

An earlier study that tried to accomplish the same purpose as that of Bouwes and Hassur (1997a) is the method proposed by Davis *et al.* (1994). The latter compared to the former, does account for both human health and environmental impacts, as well as the exposure potential of the specific chemical. In addition, this method is not site specific. However, it only includes data for 140 TRI chemicals and 21 high-volume pesticides, compared to the 345 chemicals for which toxicity weights have been assigned in the Bouwes and Hassur's (1997a) method.[16]

Based on the work by Davis *et al.* (1994), the environmental impact index is evaluated using Equations 4.7 to 4.10 (see Table 4.4)

$$\begin{aligned}\Phi = &(\text{Human Health Effect} + \text{Environmental Effect}) \times \\ &(\text{Exposure Potential})\end{aligned} \qquad (4.7)$$

$$\text{Human Health Effects} = HV_{oralD50} + HV_{inhalationLC50} + HV_{carcinogenity} + HV_{other} \qquad (4.8)$$

$$\text{Environmental Effects} = HV_{oralD50} + HV_{fishLC50} + HV_{fishNOEL} \qquad (4.9)$$

$$\text{Exposure Potential} = HV_{BOD} + HV_{hydrolisis} + HV_{BCF} \qquad (4.10)$$

where:

HV_X = hazard value for endpoint x

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[16] As of 1995, 656 chemicals are reportable under the Toxics Release Inventory. This number includes a major addition made to the TRI list in November 1994, when the EPA added 245 chemicals and chemical categories (Bouwes and Hassur, 1997).

Table 4.4: Hazard values for toxicological endpoints[17]

Toxicological Endpoint	Description	Hazard value
oral LD50	The concentration of a substance, expressed in mass of substance per mass of the animal, that will kill half a group of rodents within 14 days when administered orally as a single dose	$HV = 6.2 - 1.7\log(LD_{50})$ If $LD50 > 5{,}000$ mg/kg $\Rightarrow HV=0$ If $LD50 < 5$ mg/kg $\Rightarrow HV=5$
inhalation LC50	The concentration of a substance in air (gas or dust) that will kill half of a group of rodents when inhaled continuously for 8 hours or less, scaled to 4 hours	$HV = 8.0 - 2.0\log(LC_{50})$ If $LC50 > 10{,}000$ ppm $\Rightarrow HV=0$ If $LC50 < 31.6$ ppm $\Rightarrow HV=5$
carcinogenity	Carcinogenic effects are observed as tumors induced in an organism by exposure to a chemical, via a genotoxic or epigenic mechanism	Based on EPA or International Agency for Research on Cancer (IARC) weight-of-evidence classification[18]
other specific effects	Includes positive evidence of mutagenicity, developmental effects, reproductive effects, other chronic effects, and neurotoxicity	If evidence exist, a value of 1 is assigned to each endpoint. The hazard value is then calculated as the sum of the five endpoints for a maximum *HV* of 5
fish LC50	The concentration of a chemical in water that causes the death of 50% of the fish tested in a 96 hour test	$HV = 5.0 - 1.67\log(LC_{50})$ If $LC50 > 1{,}000$ mg/l $\Rightarrow HV=0$ If $LC50 < 1$ mg/l $\Rightarrow HV=5$ If no experimental data is available and if $\log K_{ow} \leq 6$ $\Rightarrow$[19] $HV=0$

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[17] The definitions and information in this Table is based on the *Method for Ranking and Scoring Chemicals by Potential Human Health and Environmental Impacts* (see Davis *et al.*, 1994).

[18] The EPA or IARC carcinogenic classifications consists of five groups: evidence of non-carcinogenity, not classifiable as to human carcinogenity, possible human carcinogen, probable human carcinogen, and human carcinogen. Depending on the classification of each chemical a qualitative score is assigned to the hazard value.

[19] The octanol-water partitioning coefficient K_{ow} is defined as the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase 1-octanol/water system at equilibrium (Davis *et al.*, 1994).

Table 4.4: Hazard values for toxicological endpoints (*Continued*)

Toxicological endpoint	Description	Hazard value
fish NOEL	No observable effect level (NOEL) is the highest dosage administered that does not produce toxic effects	$NOEL = fishLC_{50}/(5.3\log K_{ow} - 6.6)$ If inorganic compound $\Rightarrow NOEL = 0.05(fishLC_{50})$ If $\log K_{ow} \geq 5 \Rightarrow NOEL = 0.05(fishLC_{50})$ If $\log K_{ow} < 2 \Rightarrow NOEL = 0.25(fishLC_{50})$ $HV = 3.33 - 1.67 \log NOEL$ If $\log NOEL \leq -1.0 \Rightarrow HV=5$ If $\log NOEL > 2.0 \Rightarrow HV=0$
Biological oxygen demand (BOD) half-life	Is the number of days required for a chemical to biodegrade such that its BOD in water is decreased to half its original value[20]	$HV = 0.568 - 0.311 \ln BOD_{half-life}$ If $BOD_{half-life} \leq 4$ days $\Rightarrow HV=1$ If $BOD_{half-life} > 500$ days $\Rightarrow HV=2.5$ For metal compounds and certain inorganic chemicals in highly oxidized states $\Rightarrow BOD_{half-life} = \infty$
Hydrolysis half-life	Is the number of days required for the amount of a substance to decrease 50% its original amount through hydrolisis reaction in water at pH 7	$HV = 0.568 - 0.311 \ln hydrol_{half-life}$ If $hydrolisis_{half-life} \leq 4$ days $\Rightarrow HV=1$ If $hydrolisis_{half-life} > 500$ days $\Rightarrow HV=2.5$ For metal compounds and certain inorganic chemicals in highly oxidized states $\Rightarrow hydrolysis_{half-life} = \infty$

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[20] The BOD represents the amount of dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter (Metcalf & Eddy, 1991).

Table 4.4: Hazard values for toxicological endpoints (*Continued*)

Toxicological endpoint	Description	Hazard value
Aquatic Bioconcentration Factor (BCF)[21]	The BCF measures the chemical's ability to bioaccumulate, and it is expressed as the ratio of the concentration of a chemical in fish to its concentration in water at steady-state conditions	$HV = 0.5 + 0.5\log BCF$ If $\log BCF \leq 1.0 \Rightarrow HV=1$ If $\log BCF > 4.0 \Rightarrow HV=2.5$ $\log BCF = 0.910\log K_{ow} - 1.975\log\left(6.8\times 10^{7} K_{ow} + 1\right) - 0.786$

The last two terms in Equation 4.8 —the carcinogenity and other specific effects— account for the chronic human health effects, defined as the effects produced by a long-term, low-level exposure (Cohrssen and Covello, 1988). However, as can be seen in Table 4.4 these factors were calculated on a semiquantitave approach, where based on the carcinogenity classification or the presence of specific effects, a numerical value was assigned. However, the use of such semiquantitative evaluation might not always lead to a valid toxicity comparison between chemicals. For this reason, and by keeping the same scale assigned by Davis *et al.* (1994) to both chronic effects, the hazard value for each toxicological endpoint is calculated based on the classification presented in the Hazard Ranking System Final Rule (Federal Register, 1990) and in the Bouwes and Hassur's (1997a) methodology (see Equations 4.11 to 4.18)

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[21] The BCF is determined using the QSAR equation developed by (Bintein *et al.*, 1993). When available, experimental BCF data is to be used for inorganic chemicals.

$$HV_{other} = \max\left(HV_{RfC}, HV_{RfD}\right) \tag{4.11}$$

$$HV_{RfC} = 1.569 - 1.25 \log RfC \tag{4.12}$$

If $RfC > 18 \Rightarrow HV=0$; If $RfC < 0.0018 \Rightarrow HV=5$

$$HV_{RfD} = 1.165 - 1.167 \log RfD \tag{4.13}$$

If $RfD > 5 \Rightarrow HV=0$; If $RfD < 0.005 \Rightarrow HV=5$

$$HV_{carcinogenity} = \max\left(HV_{SF}, HV_{UR}\right) \tag{4.14}$$

$$HV_{SF-A/B} = 4.301 + \log SF \tag{4.15}$$

If $SF < 0.0005 \Rightarrow HV=1$; If $SF > 5 \Rightarrow HV=5$

$$HV_{SF-C} = 3.301 + \log SF \tag{4.16}$$

If $SF < 0.005 \Rightarrow HV=1$; If $SF > 50 \Rightarrow HV=5$

$$HV_{UR-A/B} = 4.854 + \log UR \tag{4.17}$$

If $UR < 0.00014 \Rightarrow HV=1$; If $UR > 1.4 \Rightarrow HV=5$

$$HV_{UR-C} = 3.854 + \log UR \tag{4.18}$$

If $UR < 0.0014 \Rightarrow HV=1$; If $UR > 14 \Rightarrow HV=5$

where:

RfD = chronic reference dose[22] (mg/kg-day)

RfC = chronic reference concentration[25] (mg/m^3)

SF = oral slope factor (risk per mg/kg-day)

UR = inhalation unit risk (risk per mg/m^3)

A/B = Chemical is known or is probable to be a human carcinogen under EPA's carcinogen classification system (Davis *et al.*, 1994)

C = Chemical is possible to be a human carcinogen under EPA's carcinogen classification system (Davis *et al.*, 1994)

The ranking method presented provides an estimate on the toxicity of a chemical and can be used to make comparisons among different products. However, the environmental impact index will depend on the uncertainty and availability of the required toxicological data. Some existing sources available for chemical toxicity information are presented in Table 4.5. In addition, structure-activity relationships are widely used to estimate missing data when experimental values do not exist, particularly for physicochemical endpoints and environmental effects (Davis *et al.*, 1994). These relationships are based on the assumptions that chemicals with similar molecular structures have similar physicochemical properties and biological activities.

In the case when these relationships are not available or are difficult to develop, an advantage of using the methodology proposed by Davis *et al.* (1994) is that it uses a simple scale —from 0 to 5— to evaluate the toxicological endpoints. And when toxicological data is not available for a specific chemical, a hazard value of 0 or 5 can be assigned to evaluate the sensitivity of the missing endpoint.

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[22] The specific reference doses are based on the highest dose level at which no adverse effects are observed (NOAEL) or the lowest dose level at which an adverse effect is observed (LOAEL) (Bouwes and Hassur, 1997b).

Table 4.5: Chemical toxicity information sources[23]

Description	Organization / Source
<u>ELECTRONIC SOURCES</u>	
Hazardous Substances Databank (HSDB)	Agency for Toxic Substances and Disease Registry
Registry of Toxic Effects of Chemical Substances (RTECS)	National Institute for Occupational Safety and Health
Chemical Carcinogenesis Research Information System (CCRIS)	National Cancer Institute
Genetic Toxicology	Environmental Protection Agency
Integrated Risk Information System (IRIS)	Environmental Protection Agency
Hazardous Materials Information System (HMIS)	Department of Defense
Environmental Mutagen Information Center Backfile (EMIC)	Oak Ridge National Laboratory Environmental Protection Agency National Institute of Environmental Health Sciences National Library of Medicine
Health Effects Assessment Summary Tables (HEAST)	Environmental Protection Agency
<u>LITERATURE SOURCES</u>	
Chemical Hazard Evaluation	Davis *et al.* (1994)
Toxic Release Inventory Relative Risk Based Environmental Indicators	Bouwes and Hassur (1997b)
Hazardous Chemical Data Book	Weiss (1980)
Sax's Dangerous Properties of Industrial Materials	Lewis (1996)

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[23] Most of the electronic sources can be accessed through the National Library of Medicine Toxicology Data Network (toxnet.nlm.nih.gov). IRIS is also available through the Right-to-Know Network that can be accessed on-line at http://www.rtk.net.

4.6 THE DECISION RULE

The decision rule, the last component of the decision problem, is probably the most crucial one since it facilitates the ranking of alternatives. In some cases, such as when seeking alternatives that "maximize the profit", the decision rule might be easy to formulate since one is to choose the project having the maximum possible profit. However, the decision rule might not be so clear if one seeks for example to "improve the performance of a waste water treatment facility" measured in terms of the Biochemical Oxygen Demand (BOD)[24] reduction. In this case, the decision rule might be to select alternatives that achieve a BOD level below a specified amount.

The selection of the decision rule is further complicated when the decision problem incorporates more than one objective. Since one will seldom encounter an alternative that, as is the case of the present study, "maximizes the profit" and "minimizes the environmental impact". In most cases, the decision maker must compromise one objective so as to obtain a better performance of the second one. Thus, the decision rule depends on and has to incorporate the needs and preferences of the decision maker.

Finally, the decision rule must consider the environment under which the projects are being evaluated. That is, the degree of uncertainty present in each alternative. As explained in Section 4.3, the evaluation of waste minimization alternatives will be made assuming that the decision maker has some knowledge about the process in such a manner as to predict the range within which the output of a process will fall and the frequency with which various particular outputs will be obtained.

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[24] The Biochemical Oxygen Demand (BOD) is defined as the amount of dissolved oxygen in water, that is used by the microorganisms in the biochemical oxidation of organic matter.

Given a set of m alternative actions $A = \{a_1, a_2, \ldots, a_m\}$; a set of n states of nature $X = \{x_1, x_2, \ldots, x_n\}$, where x_i is usually treated as a random variable whose probability of occurrence $\wp(x_i)$ is known or can be assumed; and a set of mn payoff values $U = \{u_1, u_2, \ldots, u_m\}$ that can be considered a function of x_i; the most common decision rule for making decisions under risk is to choose an alternative that maximizes the expected payoff value (see Equation 4.19)

$$\max_{i=1}^{m} E(a_i) = \max_{i=1}^{m} \sum_{j=1}^{n} \wp(x_j) \cdot u_{i,j}(x_j) \tag{4.19}$$

where:

$E(a_i)$ = expected value of event a_i

$\wp(x)$ = probability of occurrence of state of nature x

The payoff term in Equation 4.19 is generally expressed as a monetary value. Consequently, the problem is to select an action that maximizes the expected monetary value (EMV). However, a caveat that is often associated with this approach, is that even if it is possible to correctly assign a monetary value to each alternative evaluated, the expected value in Equation 4.19 is always assumed to be a monotonic function. That is, the attitude towards risk remains invariant regardless of the project's potential payoff. This condition might not always reflect the behavior of a particular decision maker[25]. In

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[25] This situation is better understood with the aid of an example. Suppose that an individual is given the choice to participate in a gamble based upon the toss of a coin. He is to choose between one of two alternatives:

A: There is a probability of 0.5 of winning $1,000 and a probability of 0.5 of loosing $600
B: There is a probability of 0.5 of winning $10,000 and a probability of 0.5 of loosing $5,000

this case, it might be more appropriate to employ the utility theory approach that consists in developing a utility function that reflects the preferences of the decision maker about specific alternatives in a given situation. As Park and Sharp-Bette (1990) define it, utility theory is an elegant mathematical way to describe real behavior.[26]

The most popular methods used to determine a utility function include the certainty equivalent approach, the use of indifference curves, and the use of risk coefficients (Park and Sharp-Bette, 1990). Although these methods can successfully estimate a utility function to be used in the decision making process, they are generally time consuming and quite complicated. In addition, the utility functions are developed for a particular decision maker for a given scenario. And as Luce and Raiffa (1957) state it is not meaningful to compare utilities between two people. This makes it difficult to develop a general methodology.

Even though, these methods —the utility approach and the probabilistic approach described by Equation 4.19— represent the main tools to make decisions under risk, other techniques have emerged to accomplish this task. For example, the risk adjusted discount rate method evaluates different alternatives based on risk classes. Investments that are considered to be in a safe risk class are evaluated by using an interest rate based on the cost of capital. Whereas investments with a higher uncertainty are evaluated by using a higher interest rate (Bernhard, 1984; Park and Sharp-Bette, 1990). However, a controversy exists about the choice of an appropriate adjusted discount rate factor.

In this case, the expected monetary value —based on Equation 4.19— is of $200 and $2,500 for alternatives A and B respectively. Hence, it is expected that the individual will choose alternative B. However, not all individuals are willing to take the chance of loosing $5,000.

[26] A detailed description of utility theory can be found in several sources including: French (1986), Luce and Raiffa (1957), and Park and Sharp-Bette (1990).

A second approach that is worth mentioning is fuzzy decision analysis[27]. As described by Zimmermann (1987:11), fuzzy set theory "provides a strict mathematical framework in which vague conceptual phenomena can be precisely and rigorously studied." This implies, that it is possible to incorporate concepts where partial truth and partial falsity —that is an object does not necessarily have or do not have a specific property— exist simultaneously and to recognize that the transition between these two phases can take place (Franz *et al.*, 1995).

Fuzzy sets can be used in business decision making whenever precise numbers or relationships cannot be determined (Korvin *et al.*, 1995). However, a comparison of fuzzy and probabilistic programming models favors the use of the latter, even when the complete probability distributions of the random parameters are unavailable (Liu and Sahindis, 1996). In addition, as Chessman (1986) argues, probability theory is quite adequate for many of the problems addressed by fuzzy logic and often requires specifying fewer parameters.

Based on the previous discussion, the decision rule applied in this work is based on a probabilistic approach (see Equation 4.19) applicable in the analysis of stochastic processes, that can be defined as "families of random variables, dependent upon a parameter which usually denotes time" (Parker, 1994, p. 220).

As can be seen from Equation 4.19, the expected value of a random variable is obtained by finding its average response over all its possible values. Consequently, one needs to know all the values that the random variables can take and their corresponding

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[27] Fuzzy decision analysis based on the concepts of fuzzy mathematics has been applied in a wide variety of disciplines including decision making A survey of recent developments in fuzzy programming is given by Inuiguchi *et al.* (1990).

payoffs. However, the analyst seldom has knowledge about the complete random variable distribution, and estimating such distribution if feasible, is generally time and computationally intensive. Furthermore, in some instances the experiments required to estimate the population can be quite expensive from an investment point of view. Therefore, the approach taken is to obtain a sample from the population and use statistical inference techniques to get an estimate of the different parameters, such as the expected value. And once the sample has been taken, the expected value is said to be enclosed within the following range:

$$E(a_i) \pm t_{\alpha_s/2;n_s-1} \frac{\sigma}{\sqrt{n_s}} \tag{4.20}$$

where:

σ = sample standard deviation

n_s = sample size

$t_{\alpha_s/2;n_s-1}$ = value on the *t*-distribution with n_s-1 degrees of freedom such that the area to the right of it is $\alpha_s/2$ (Pfaffenberger and Patterson, 1987)

The value of the *t*-distribution is used to represent the confidence interval and its values can be obtained from *t*-distribution tables available in most statistics texts.

4.7 SUMMARY

This chapter presented the description of the initial step within the alternative's evaluation phase. Under the framework of decision making, this chapter discusses each of the five key components of a decision problem, that as was shown in Figure 4.1 need to be specified before continuing on to the optimization of source reduction alternatives. In summary, the main ideas to be taken out of this chapter include:

- The statement of the decision problem initiates with the *identification of the decision making unit* who determines which if any of the alternatives is to be implemented. In this work, the decision to implement a pollution prevention project is assumed to be made by a single person.
- Decisions can be made under conditions of certainty, risk, uncertainty, or under a combination of the last two. In general, when dealing with uncertainty some amount of information is available or can be assumed. Therefore, in this work *the evaluation of source reduction alternatives will be made using methods suitable for making decisions under risk.*
- The analysis of source reduction alternatives is evaluated using two competing objectives: *"maximize profit" and "minimize environmental impact."*
- The profit is measured using the *annual equivalent profit (AEP)* taking into account the revenue obtained, the manufacturing costs, and the environmental benefits and costs. The details of how these costs are calculated are given in Chapter 5.
- The environmental impact is measured using *a non-monetary valuation technique that incorporates toxicological data* and by including *a release factor* that is equivalent to calculating the probability of obtaining a release from a specific stream.

- The *decision rule* that facilitates the ranking of the alternatives used is based on a *probabilistic approach*, selecting the alternative that maximizes or minimizes the expected value.

CHAPTER 5

ENVIRONMENTAL ECONOMICS

The previous chapter focused on the initial step within the alternative's evaluation phase: the statement of the decision problem. As can be seen in Figure 5.1, this chapter continues this discussion, describing in detail how the benefits and costs associated with a particular investment project are estimated. These costs are then used to evaluate the annual equivalent profit, one of the two objectives used to compare process alternatives.

5.1 INTRODUCTION

Since the concept of waste minimization was first introduced as a national policy in the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA), voluntary programs by the Environmental Protection Agency (EPA) and other agencies and organizations have looked at ways to encourage pollution prevention through source reduction instead of the traditional end-of-the-pipe treatment approach. Attempts have been made to promote within industry the benefits of applying waste reduction programs, that include savings in waste management costs, reduction in the use of raw materials, and minimization of potential environmental liability. However, despite these and other benefits a report by the EPA (EPA, 1992)

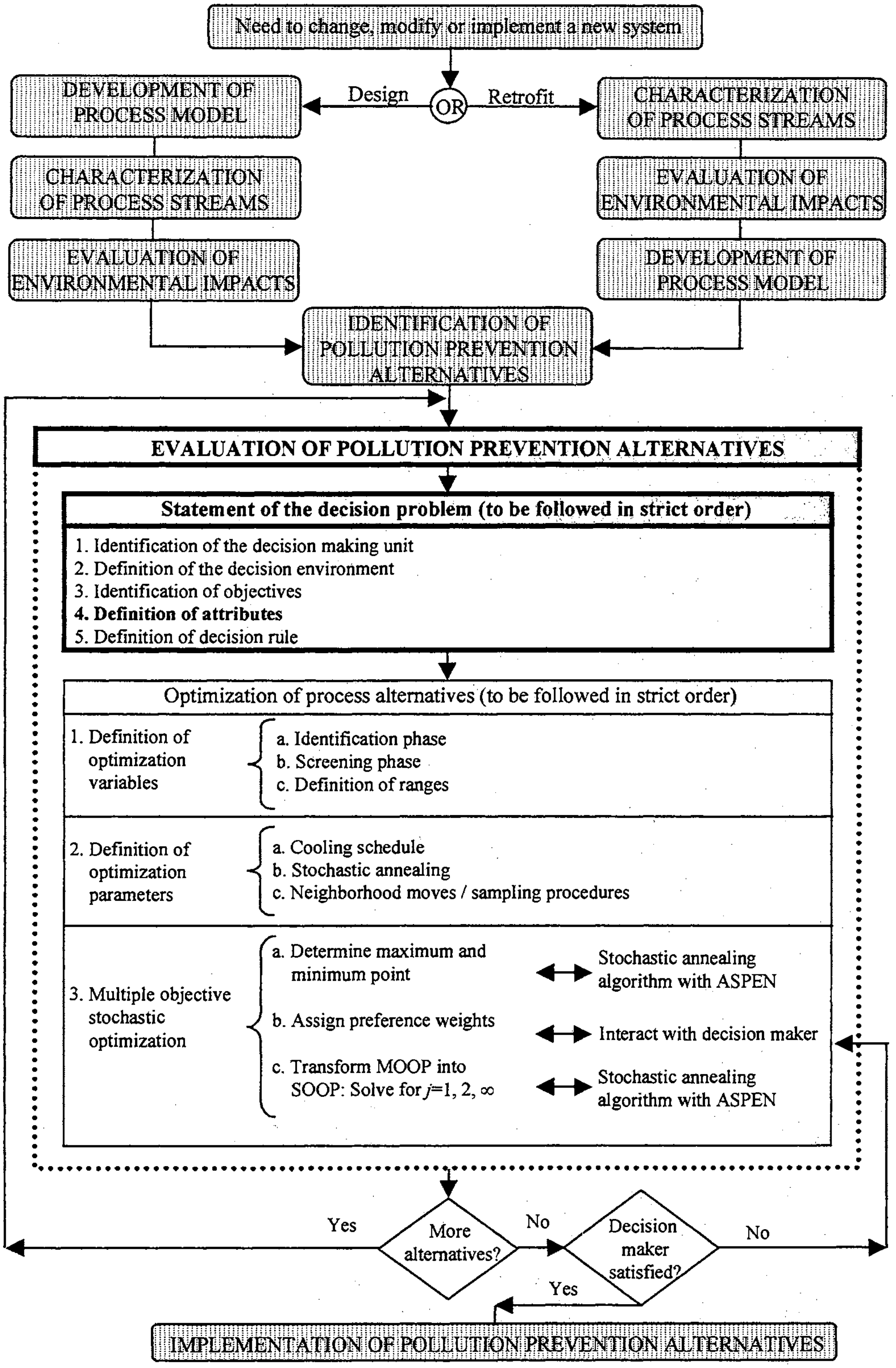

Figure 5.1: Road map[1] - Chapter 5

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[1] Lines/text in bold: topics discussed in this chapter. Shadow boxes: topics discussed in previous chapters.

suggests that the majority of U.S. manufacturers have been slow to move away from traditional end-of-the-pipe strategies. The main reason for this lies in the fact that environmental costs are usually difficult to determine and are very often underestimated.

The underestimation occurs when firms incur environmental costs that are not linked to processes and products, and are treated as part of the overhead expenses. For example, in a survey conducted for the EPA, for a range of 17 environmental costs over half of the respondents report initially assigning environmental costs always to overhead accounts. However, 58% of those who initially assign costs to an overhead account later relocate them to a product or process (EPA, 1995a). As a consequence of this misallocation, the decision maker does not get a clear picture of where and how costs are generated (EPA, 1995a). This information is crucial for industry to make an objective decision regarding the feasibility of a pollution prevention project. Therefore, the decision making process where pollution prevention projects are compared against other possible investments, fails in making a valid comparison. In this context, it is important to be able to account for the different environmental costs that can be considered to include two separate dimensions (EPA, 1995b): societal costs and private costs.

Societal or damage costs include the costs to individuals, society, and the environment. They represent the impacts on the environment and society for which the company is not legally accountable[2]. They include the environmental degradation and the adverse impacts on human beings, their property, and their welfare.

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[2] Even though, firms are usually not legally liable for these costs, within the realm of international environmental law, companies need to follow the Polluter Pays Principle (PPP). This principle —introduced in 1990 as a global treaty— originally meant that "the polluter shall bear the cost of pollution prevention and control measures required so that the environment is in an acceptable state" (Smets, 1994). According to PPP, costs to be borne by the polluter cover the damage costs, the costs of pollution prevention, and the costs of control and reduction measures, including those that seek to avoid the release

On the other hand, private costs includes the costs which the company incurs and have a direct impact on its bottom line (i.e. capital equipment, materials, utilities, etc.). At this level is where companies traditionally begin to implement environmental accounting, or what is referred to as total cost assessment (TCA)[3]. Compared to traditional accounting methods, TCA includes all environmental or waste related costs and benefits as part of the capital budgeting decision.

The costs and benefits that are to be included within the environmental accounting framework can be divided in increasing complexity in five groups: (1) usual costs, (2) direct costs, (3) hidden costs, (4) liability costs, and (5) less tangible benefits. In this work, these five groups will be used to measure the alternative's profit and consequently determine its AEP.

5.2 USUAL COSTS

The usual costs include the total fixed capital investment and the production costs generally associated with the process or product. The total fixed capital investment is the amount of money required to supply the necessary equipment and manufacturing facilities[4], plus the amount of money required as working capital[5] for operation of these

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of pollutants, of controlling such releases, and of taking further measures to reduce the effects of pollutants that are released to the environment (Smets, 1994).

[3] TCA as defined by the EPA is a "generic term for the long-term, comprehensive analysis of the internal costs and savings of pollution prevention and other environmental projects" (EPA, 1996c).

[4] Peters and Timmerhaus (1991) present ranges and typical values for capital investment items as a percentage of the purchased equipment or fixed capital investment. These figures represent typical numbers and may vary depending on the particular application. In addition, when evaluating source reduction alternatives especially in the case of retrofit projects, not all items need to be included.

[5] The working capital is the amount of money invested in raw materials, supplies, and finished products in stock; semifinished products in the manufacturing process; accounts payable and receivable; taxes payable; and cash amounts necessary for monthly payments of operating expenses (Peters and Timmerhaus, 1991).

facilities, plus the cost of land and other non-depreciable costs (Holland and Wilkinson, 1997) (see Equation 5.1)

$$C_{TC} = C_{FC} + C_{WC} + C_{L} \tag{5.1}$$

where:

C_{TC}= Total fixed capital investment

C_{FC} = Fixed capital investment

C_{WC} = Working capital

C_{L} = Cost of land and other non-depreciable costs

Assuming that the working capital corresponds to a value of 15% of the total fixed capital investment (Douglas, 1988)[6], Equation 5.1 can be formulated as a function of the purchased equipment costs (see Equation 5.2)

$$C_{TC} = \frac{(1+\alpha)(1+\beta)}{0.85} C_{PE} \tag{5.2}$$

where:

C_{PE} = Purchased equipment costs

α = Direct cost correction factor

β = Indirect cost correction factor

Based on the ranges and information presented by Peters and Timmerhaus (1991), the direct cost and indirect costs correction factors in Equation 5.2, can vary between values of 1.05 to 3.58 and 0.15 to 0.30 respectively. Typical values for

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[6] An alternative estimate of the working capital can be made taking a 3 month supply of raw materials or product (Douglas, 1988).

α depending on the type of project and processing plant are shown in Table 5.1. However, in some cases such as in small retrofit projects, α and β can have smaller values as $\alpha \rightarrow 0$ and $\beta \rightarrow 0$.

Once the purchased equipment costs are calculated, a rough estimate of the total fixed capital investment can be obtained using Equation 5.2. There are several methods that can be used to estimate these purchased equipment costs, a review of them is given by Holland and Wilkinson (1997). Whichever method is employed to estimate the capital investment, it is usually based on time sensitive information. In this case, the cost indexes (see Equation 5.3),

Table 5.1: Typical values for the direct cost correction factor[7]

	α
Solid-fluid processing plant	
New plant at new site	2.20 ± 0.4
New unit at existing site	2.02 ± 0.4
Expansion at an existing site	1.80 ± 0.4
Fluid processing plant	
New plant at new site	2.53 ± 0.4
New unit at existing site	2.13 ± 0.4
Expansion at an existing site	2.14 ± 0.4
Solid processing plant	
New plant at new site	2.26 ± 0.4
New unit at existing site	1.83 ± 0.4
Expansion at an existing site	1.73 ± 0.4

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[7] The range (± 0.4) in the values tabulated for α depends on the estimates used for the installation of the equipment and the cost of service facilities. The latter cost might vary depending on the existing and available service facilities. When dealing with projects where no land or yard improvements are required, 0.21 should be subtracted from the value of α.

$$C_p = C_0\left(\frac{i_p}{i_0}\right) \tag{5.3}$$

where:

i_0 = original index value

i_p = index value at present time

C_0 = original capital cost

C_p = capital cost present value

such as the Marshall and Swift Equipment Cost Index (M&S), and the Chemical Engineering Plant Cost Index (CE), can be used to update the information obtained from the cost correlations or when capital cost data is available from some time in the past.

The production costs —the second realm of the usual costs— include all the expenses related to the manufacturing operation[8]. As for the case of capital costs, there are several methods or sources available to estimate the manufacturing costs expressed on an annual basis, a review of them is presented by Holland and Wilkinson (1997). For example, raw materials and solvent costs can be found in the *Chemical Marketing Reporter*. Power and utilities cost can be obtained from company data or if fuel prices are known, they can be used as a factor to estimate different utilities as shown in Douglas (1988). Operating labor and supervision expenses can be estimated based on the total product cost, and maintenance outlays can be a function of the total capital investment.

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[8] Manufacturing cost items include for example: raw materials, operating labor and supervision, power and utilities (steam, electricity, fuel, refrigeration, and water), maintenance and repairs, operating supplies, catalysts and solvents, and laboratory charges (Peters and Timmerhaus, 1991).

5.3 DIRECT COSTS

The direct costs include the capital, operating, material, and maintenance costs involved in the treatment, recycling, handling, transportation, and disposal of waste. Within the EPA regulations, waste is defined as "anything produced by a process or by accident, which cannot be directly used onsite as a raw material for another process without some sort of treatment. A waste is also any material which cannot be reused onsite at all, and must be sent off for disposal or processing into another product or raw material. Chemicals which are off-specification, or become so due to age, are also wastes" (Carlson, 1992, p. 85).

A waste identification study performed as part of the characterization of process streams' phase is required to identify the waste streams within a process and consequently identify their direct costs. However, when evaluating a process alternative, a possible confusion may arise between what to consider as usual costs and what to consider as direct costs. In this context, what is important is not the classification *per se*, but the fact that the necessary information has been included in the decision making process.

The waste identification and characterization study together with the information obtained during the evaluation of environmental impacts is used to estimate the direct costs of a process (see Equation 5.4).

$$\begin{aligned} W &= \sum_{i=1}^{n}\sum_{j=1}^{m} w_i m_{j,i} c_j + \sum_{i=1}^{n} w_i \left(Tr_i + M_i d_i + D_i\right) \\ &= \left\{\begin{matrix}\text{loss of material} \\ \text{being wasted}\end{matrix}\right\} + \left\{\begin{matrix}\text{treatment} \\ \text{cost}\end{matrix}\right\} + \left\{\begin{matrix}\text{transportation} \\ \text{cost}\end{matrix}\right\} + \left\{\begin{matrix}\text{disposal} \\ \text{cost}\end{matrix}\right\} \end{aligned} \tag{5.4}$$

where:

W = Direct waste cost

w_i = Flowrate of waste stream i

$m_{j,i}$ = Mass fraction of component j in waste stream i

c_j = Cost of component j

Tr_i = Treatment cost

M_i = Transportation cost to waste treatment or disposal facility

d_j = Distance to waste treatment or disposal facility

D_j = Disposal cost

The first term in Equation 5.4 represents the loss of material being wasted within a particular process stream. This includes, for example the cost of raw materials or product that is being released to the environment as a component of a waste stream, instead of being converted into finished product and subsequently becoming a source of income. In this manner, the true cost of the waste stream can be accounted for.

The treatment cost[9] *Tr* in Equation 5.4 includes the manufacturing costs and the required fixed capital investment for the treatment of waste. This treatment can eliminate, partially or completely all environmental damage costs. For example, as can be seen in Figure 5.2, when environmental contamination approaches zero, treatment costs are maximum and damage costs are minimum. Therefore, a decision needs to be

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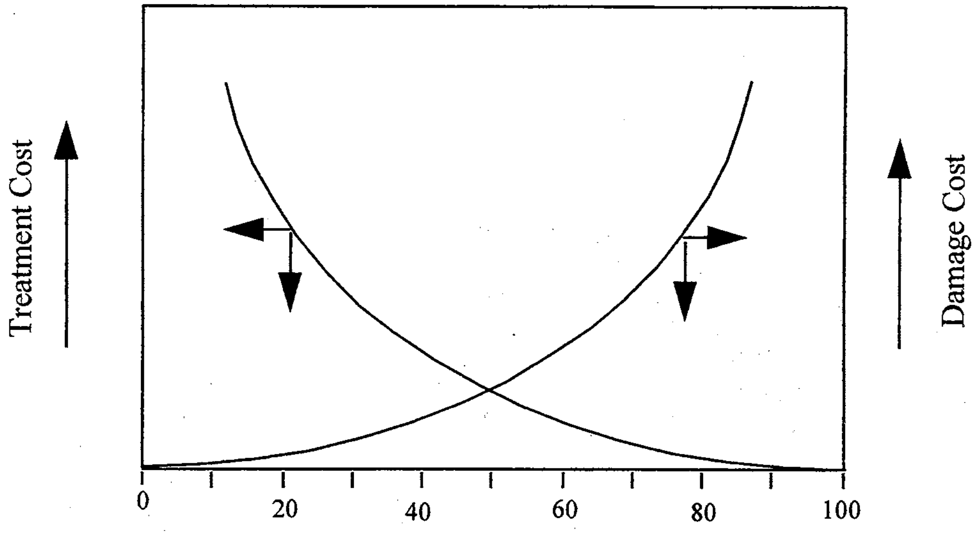
[9] The treatment of waste within a processing facility may require a special RCRA permit. Under which the facility will be considered as a treatment facility with additional regulatory requirements. A facility may be exempted from such permit under the following guidelines: (1) totally enclosed treatment facility, (2) elementary neutralization unit, (3) permit-by-rule, (4) discharges to a Publicly Owned Treatment Works (POTW), and (5) direct discharge to surface waters (see Beranek and Lamm, 1992).



Environmental Contamination (%)
Figure 5.2: Optimum degree of treatment (Nemerow, 1995)

made regarding the optimum degree of treatment required; since an excess may not be economically feasible, while on the other hand too little treatment can result in excessive damage costs. Furthermore, the degree of treatment applied to a particular waste stream is also influenced by the current regulatory scheme (see Table 5.2).

Once the degree of treatment required is defined, a specific treatment technology should be selected that can achieve the necessary reduction in environmental contamination. Noyes (1994) presents a comprehensive review of treatment technologies. Similar reviews and comparison studies are given by Corbitt (1990); Dyer and Mulholland (1994); LaGrega *et al.* (1994); Sittig (1993); Theodore *et al.* (1997); Metcalf & Eddy (1991); Bouwes and Hassur (1997a); and Cooper and Alley (1994). In addition, EPA information sources, such as the *Pollution Prevention Information Clearinghouse* (PPIC) and the *Alternative Treatment Technology Information Center* (ATTIC) (EPA, 1995c) are also available.

Table 5.2: Selected regulations applicable to the industrial sector[10]

Type of emissions	Selected applicable regulations
Air	Companies need to comply with the maximum available control technology (MACT) emission standards for the 189 hazardous air pollutants (HAP) included in the Clean Air Act. MACT standards require the maximum degree of emission reduction that is economically feasible. These standards to be set before the year 2000, are applicable to over 350 different source categories considered as major point sources.[11]
Water	For discharges to surface water and navigable waters, industry needs to adhere to the regulations set forth in the National Pollutant Discharge Elimination System (NPDES) within the Clean Water Act. This act covering 129 toxic pollutants has the purpose of restoring and maintaining the chemical, physical, and biological integrity of the Nation's waters (Jain, 1990). In addition, discharges into municipal sewer plants are required to adhere to pretreatment standards.
Hazardous waste	Processing facilities need to comply with the requirements established in the Resource Conservation and Recovery Act (RCRA) for the generation, transportation, storage, treatment, and disposal of hazardous waste. A waste is considered to be hazardous when it exhibits one of four specific characteristics (ignitability, corrosivity, reactivity, and toxicity) , or by being listed within four lists (designated as the “F”, “K”, “P”, and “U” lists). These lists include waste chemicals from nonspecific sources, byproducts of specific industrial processes, and pure or off-specification commercial chemical products (Jain, 1990).

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[10] The regulations included in this table represent the ones having the greatest possible impact in a plant operation. However, there are many other that might be applicable to a particular operation. A review of them can be found for example in Theodore *et al.* (1997). In addition, a regulatory update related to the CPI is published monthly by *Chemical Engineering Progress*.

[11] Major point source is defined as a facility emitting more than 10 ton/year of any HAP, or 25 ton/year of any combination of HAP (Phillips and Lokey, 1992).

The capital investment and operating costs of waste treatment facilities, can be estimated using similar methods as the ones applied for the case of the usual costs. In addition, several sources are available that present estimates of waste treatment options (see Table 5.3). In addition, correlations are available for estimating the capital cost of waste treatment equipment including ASPEN PLUS™ costing module for general unit operations and treatment equipment; Peters and Timmerhaus (1991) for general unit operations and material handling and treatment equipment; Cooper and Alley (1994) for air pollution control equipment; and Benjes (1980) for biological waste treatment processes and equipment. Finally, the EPA offers several information sources and databases that can be used to obtain additional waste treatment information (EPA, 1995c).

Cost indexes, such as the Marshall and Swift Equipment Cost Index (M&S), and the Chemical Engineering Plant Cost Index (CE) can also be used to determine the cost of waste treatment equipment, if past information is available. However, as Vatavuk (1995) suggests such indexes might not be appropriate for estimating the costs of air pollution control equipment. For this case, Vatavuk (1995) presents cost indexes (see Equation 5.4) to determine prices for 11 classes of gaseous and particulate control devices.

The transportation and disposal costs terms in Equation 5.4, can be an important factor in the waste cost determination. Estimates for these costs depend on the particular process facility and on the type of waste under consideration. For example, Cressman and Martin (1993) present cost data for hazardous waste disposal fees (including analysis costs) and surcharges for polychlorinated biphenyl (PCB) and non-PCB containing waste.

Table 5.3: Summary of selected sources for waste treatment costs

Source	Description
Nemerow and Dasgupta (1991)	Present a summary of waste treatment costs for several treatment methods within different industry sectors; including, the oil refinery, fuel wastes, the chemical industry, the explosive industry, the pesticide industry, the resins and plastics industry, and the energy industry.
Dyer and Mulholland (1994)	Present estimates for the minimum capital investment and costs for the treatment of simple organic waste gas streams as a function of flowrate. In addition, expected values are given for simple and complex waste gas streams containing particulates and chlorocarbons.
Cressman and Martin (1993)	Display costs for five stabilization/solidification[12] scenarios: in-drum mixing, in-situ mixing, mobile plant mixing of pumpable/umpumpable materials, and area mixing. The data introduced includes various cost parameters and the comparison of treatment costs with different reagents.
DuTeaux (1996)[13]	Compiles cost information for environmental remediation technologies used in the treatment of hazardous, radioactive, and mixed wastes. Technologies reviewed include biological treatments, physical/chemical treatments, and thermal treatments for the remediation of soil, sediment, sludge, groundwater, and surface water.

Finally, an important factor to consider in the treatment, transportation, and disposal costs is that of the mixing rule associated with waste management operations. In this context, a non-hazardous waste if mixed with a small amount of a hazardous substance, is to be considered a hazardous material for which the related regulations apply. Therefore, in some instances it might be appropriate to have separate waste management operations for hazardous and non-hazardous wastes.

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[12] Stabilization systems attempt to reduce the solubility or chemical reactivity of the waste by changing its chemical state or by physical entrapment. Solidification systems attempt to convert the waste into an easily handled solid with reduced hazards from volatilization, leaching or spillage (Cressman and Martin, 1993).

5.4 HIDDEN COSTS

The hidden costs include the expenses associated with permitting, monitoring, testing, training, inspection, and other regulatory requirements related to waste management practices (see Table 5.4). These costs can have an important impact on the environmental accounting analysis and are generally not allocated to the unit responsible for incurring them. They are usually charged to an overhead account (EPA, 1989).

In comparison with the previous cost categories —usual and direct costs—, the hidden costs are generally not a direct function of the amount of waste being generated. This situation might initially inhibit the use of this phase as a tool to analyze source reduction alternatives. However, some regulation requirements that can have a big impact on the environmental costs might be triggered with the use of a specific chemical. In addition, the hazard characteristic of the process or the amount of hazardous or non-hazardous waste being handled can influence the hazardous waste generator classification, and thus, become an important source of environmental costs.

In summary, the hidden costs are influenced and will rely upon the specific regulatory requirements of the existing operation, as well as on the future requirements needed when implementing a selected alternative process. Hence, in order to identify these costs the regulatory status of the facility needs to be identified.[14] Based on this determination, the fixed capital and the hidden expenses in Table 5.4 can be specified.

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[13] The compendium by DuTeaux (1996) can be accessed on-line at *http://www.lanl.gov/projects/ecap/*

[14] The regulatory status identification process can vary depending on the facility and process characteristics. EPA (1989) presents a questionnaire that can be used to determine this status and is useful for identifying the specific requirements included as part of the hidden costs classification. In addition, there are several software packages, such as Audit Master, that find the regulatory framework governing a

Table 5.4: Items included in the hidden costs (EPA, 1989)

Fixed capital	Expenses	
• Monitoring equipment • Preparedness and protective equipment • Additional technology • Other	• Notification • Reporting • Monitoring/testing • Recordkeeping • Planning/studies/modeling • Training • Manifesting	• Labeling • Preparedness and protective equipment • Closure/post closure care • Medical surveillance • Insurance/Special taxes • Inspections

The fixed capital —within the hidden cost group— is required to satisfy the technology-forcing or minimum-technology requirements currently being enforced as a part of specific regulation.. For example, these requirements might include treatment standards for hazardous wastes and technology requirements for land disposal. In addition, future technology obligations need to be considered as part of the evaluation study.

The fixed capital investment needed to comply with the technology forcing requirements might already have been considered as part of the usual or direct costs. As was previously discussed, what is important is to account for these costs, independent of the cost category. Nevertheless, once the technology forcing requirements have been identified, the fixed capital can be estimated as was done in the case of the usual costs.

The expenses in Table 5.4, associated with the hidden costs can be calculated using Equation 5.5 (EPA, 1989).

$$H_x = f_H\left(m_H + t \cdot s\right) \tag{5.5}$$

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specific facility (Grinthal, 1993b). Furthermore, a regulatory assessment study can be solicited. This study, as suggested by Dyer and Mulholland (1994), can range between $1,000 and $2,500.

where:

H_x = expenses of item x (see Table 5.4)

f_H = frequency of occurrence per year

m_H = non-labor costs

t = time required (hours per occurrence)

The variables used to calculate the hidden costs in Equation 5.7 are a function of the regulatory status of the project under evaluation. Summarizing the information presented by EPA (1989), approximate values for the variables in Equation 5.7 are presented in Appendix B for each type of regulation, including RCRA, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Superfund Amendments and Reauthorization Act (SARA) Title III, CAA, CWA, and the Occupational Safety and Health Act (OSHA). Based on this information and depending on the regulatory status of the facility and the specific operation environment, the hidden expenses, can range from \$10,000 to \$110,000 per year. This range does not include all the expenses presented in Table 5.4, since some of them require specific site, chemical, and/or operations information, for which no estimates values are included in Appendix B. In addition, no estimates are given for permitting costs for which federal, state, or local regulations might apply. In any case, when detailed information regarding the hidden costs is available it should be included as part of the financial investment analysis.

5.5 LIABILITY COSTS

Liability costs include the fines and penalties to be incurred when a facility is in non-compliance with environmental regulations. In addition, these costs incorporate the future liabilities for remedial action, personal injury, and property damage associated with routine and accidental releases of hazardous substances.

Even though these costs can be very significant, their estimation is an area fraught with uncertainty. Therefore, due to a lack of accuracy in their determination these costs are usually not included as part of the decision making process. For example, in a study conducted for the EPA only 57% of the respondents include environmental penalties and fines in their financial evaluation process (EPA, 1995a).

The liability costs can be divided in two groups: (1) penalties and fines, and (2) future liabilities. Both of these are judgmental in nature and will require a probabilistic evaluation of future events associated with the process in operation.

5.5.1 PENALTIES AND FINES

The penalties and fines due to non-compliance can be estimated using EPA's BEN model (EPA, 1993) that calculates the economic benefit that a violator obtains from delaying or avoiding the compliance with environmental regulations. Even though the penalty figure is easy to obtain once the required input is available —that sometimes is not so easily identified—, the BEN model can lead to incorrect and generally exaggerated estimates (Wise *et al.*, 1992). In addition, when comparing process alternatives the BEN model might not be the best methodology to employ, since it is based on evaluating the process' past compliance, making it difficult to correctly evaluate possible future process improvements.

In the present methodology, a second method is used that might be more appropriate for comparing alternative projects. This method is based on probability estimates of the expected annual penalties and fines associated with each regulation (see Equation 5.6).

$$E(k_f) = \sum_{i=1}^{n} k_{f,i} \cdot \wp(k_{f,i}) \tag{5.6}$$

where:

$E(k_f)$ = Expected value of fines and penalties

k_f = Fines and/or penalties for the non-compliance of an environmental regulation

$\wp(k_f)$ = Probability[15] of falling in non-compliance and having the obligation to pay the fine and/or penalty k_f

The information required to calculate $E(k_f)$ can be estimated using knowledge of existing plant operations and/or some knowledge of previous penalties imposed to the facility. When pertinent information is not available, Table 5.5 can be used as an estimate of the fines and/or penalties term.

To apply Equation 5.6 the value of k_f can be used as the median number in Table 5.5. However, an alternative approach is to consider the probability of having to pay the fines and penalties in the lower range and the probability of falling in the higher range. In this case, the expected value of penalties and fines is calculated using Equation 5.7.

$$E(k_f) = \sum_{i=1}^{n} \left[k_{f-low,i} \cdot \wp(k_{f-low,i}) + k_{f-high,i} \cdot \wp(k_{f-high,i}) \right] \tag{5.7}$$

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[15] In most cases, the probability term corresponds to a subjective approach in which the "probability is taken as representing the observer's degree (or strength) of belief that the system will adopt a certain state." (French, 1986, p. 222).

Table 5.5: Example of selected penalties and fines (EPA, 1989)[16]

Regulatory program	Penalties/Fines ($)		
	Low	High	Median
RCRA	500	115,000	7,550
CAA (Stationary source)			
Judicial	--	600,000	65,750
Administrative	1,270	1,270	1,270
CWA	--	1,000,000	50,000
SDWA			
Judicial	1,000	6,200	3,000
Administrative	2,050	10,000	--
TSCA	--	1,000,000	1,300
FIFRA	--	25,000	780

where:

$k_{f\text{-}low}$; $k_{f\text{-}high}$ = Fines and/or penalties for the non-compliance of an environmental regulation in the lower and higher range respectively

$\wp(k_{f\text{-}low})$; $\wp(k_{f\text{-}high})$ = Probability of falling in non-compliance and having to pay the fine and/or penalty in the lower or higher range respectively

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[16] Table 5.5 presents only an example of selected penalties and fines for the fiscal year 1987. Translating these values into today's dollars should be done carefully since they are a function of the current regulatory environment governing the penalties and fines guidelines.

5.5.2 FUTURE LIABILITIES

The future liabilities, considered as the liability costs' second group, incorporates the liabilities associated with remediation, compensation, and natural resource damages.[17]

- Remediation obligations for cleaning up existing environmental contamination and potential future contamination sites can be very expensive, ranging up to several millions of dollars (EPA, 1996d). They may arise as future costs resulting from inactive waste sites —referring to activities that have ceased to be in operation—, active waste sites, and future remediation responsibilities related to activities that have not yet started (i.e., liabilities resulting from accidental releases during transport of hazardous waste, liabilities due to future spills at fixed facilities, and liabilities from existing and future leaks from underground storage tanks).
- Compensation liabilities —that may arise from past, continuing, and future activities— are related to common law under which "companies may be obligated to pay for compensation of damages suffered by individuals, their property, and business due to the use or release of toxic substances or other pollutants." (EPA, 1996d, p. 11). These liabilities may occur regardless of the company's environmental compliance status.

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[17] The activities included as part of the future liabilities, such as landfill releases, might not be directly managed or in control of the facility for which a source reduction project analysis is being made. However, the company might still be liable for them according to the "potentially responsible party" principle within the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). CERCLA, better known as Superfund, establishes that the persons responsible for cleaning up a contaminated site include: "(1) the owner or operator of the site, (2) any person who owned or operated the site at the time the hazardous substances were deposited there, (3) any person (generator) who arranged to have his own waste taken to the site for disposal or treatment, and (4) any person who transported waste for disposal or treatment to a site he selected" (Schworer and Dean, 1992:408).

- Natural resource damages liability established under the CWA section 311, CERCLA section 107, and Oil Pollution Act (OPA) section 1006 relates to injury, destruction, or loss of use of natural resources that do not constitute private property (EPA, 1996d). These damages can occur from the accidental or normal releases that can subsequently affect the flora, fauna, land, air, and water resources. However, despite their importance, most natural resource damage payments have been relatively small according to the EPA (1996d).[18]

Not many methods are available to estimate the future liabilities. However, a review of several of them is presented by EPA (1996d). The methods available have usually been designed to study one of the future liabilities' category under a given scenario. In addition, some of the existing methods rely on data obtained from specific case studies, while others present only a methodology where no specific data or algorithm is given to calculate liability costs. Furthermore, for some release scenarios (e.g., compensation liabilities due to continuing or accidental releases to air and water) no valuation techniques have been reported in the literature. Hence, due to the uncertainty associated with the determination of future liabilities costs as well as the lack of a general methodology to estimate them, the approach proposed in the present work is similar to the one used for the case of fines and penalties (see Equations 5.8 to 5.10).

$$E(k_r) = \sum_{i=1}^{n} k_{r,i} \cdot \wp(k_{r,i}) \tag{5.8}$$

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[18] Based on a report by the General Accounting Office of 98 cases settled by federal trustees, 48 cases were settled for zero dollars, 36 cases for less than $500,000 each, 9 cases for between $500,000 and $5 million, and 5 cases for greater than or equal to $12 million (EPA, 1996d).

$$E(k_c) = \sum_{i=1}^{n} \wp(k_{c,i})\left[L_{c,i} + c_{L,i}k_{c,i}\right] \tag{5.9}$$

$$E(k_N) = \sum_{i=1}^{n} k_{N,i} \cdot \wp(k_{N,i}) \tag{5.10}$$

where:

$E(k_r)$ = Expected value of remediation costs

k_r = Remediation costs incurred in the event of a release

$\wp(k_r)$ = Probability of a release from a particular operation

$E(k_c)$ = Expected value of compensation costs

k_c = Compensation costs incurred in the event of a claim given a release

$\wp(k_r)$ = Probability of a claim given a release from a particular operation

L_c = Legal defense costs

c_L = Percentage of the claims that require compensation payments

$E(k_N)$ = Expected value of the natural resource damages

k_N = Natural resource damage expenses to be paid if a release occurs

$\wp(k_r)$ = Probability of incurring in natural resource damages given a release from a particular operation

The information required to estimate the expected values of the future liabilities in Equations 5.8 to 5.10 depends on the process or operation being evaluated. Some knowledge of previous cases handled within the company might be helpful in evaluating these costs, or in some instances information regarding similar cases can be obtained from EPA's Civil Docket Database[19]. In addition, a summary of typical values taken by these variables is presented in Table 5.6, where the dollar figures correspond to the average values expected from several release scenarios. For obligations related with operating facilities and accidental releases from such facilities, the probability of a release can be estimated using the classification given previously in Table 4.3 or using the fire and explosion index developed by Dow Chemical company (Gowland, 1996).[20]

Finally, for the case of natural resource damages the information presented in EPA (1996d) can be used to calculate the expected value as was done with the fines and penalties (see Equation 5.7) using the information given in Table 5.7. In any case, the values employed to calculate the future liabilities will depend on the specifics of the process and on the judgment of the decision maker.

5.6 LESS TANGIBLE BENEFITS

The less tangible benefits, the last group within the environmental framework, include the benefits obtained as a result of the increase in revenues or decrease in expenses due to an improvement in consumer acceptance, employee relations, and corporate image. The corporate image may deteriorate not only due to bad waste management practices. Current and future environmental regulations, such as EPA's Risk Management Program (RMP) [21] might have an indirect impact on the company's image.

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[19] The DOCKET database accessible on-line through the RTK network at *http://www.rtk.net* contains records about all civil cases filed by the Department of Justice on behalf of the EPA.

[20] Even though this method provides a comparative measure of the overall risk of fire and explosion of a process, the index can be used to compare the possibility of a release from specific process operations.

[21] As part of the RMP requirements companies need to perform a worst-case scenario analysis of their operations. The result of this analysis must be made available to the general public by June 1999 (Carroll and Russell, 1999).

Table 5.6: Future liabilities cost information[22]

Process / activity	$\wp(k_r)$	k_r	$\wp(k_c)$	c_L	L_c	k_c
Release from storage drum[23]	0.001	3.26 $/ton 500 $/release	0			
Release from storage tank	0.00116	On site: $10,100 /release 6.68 $/ton if $ST<$ 90 d 32.6 $/ton if $ST>$90 d Regional: $10,100 /release 6.68 $/ton if $ST<$ 90 d 32.6 $/ton if $ST>$90 d	0.10	0.20	$60,000	On site: 1,000,000 $/claim 0.25 $/ton if $ST<$ 90 d 0.85 $/ton if $ST>$90 d Regional: 1,000,000 $/claim 0.04 $/ton if $ST<$ 90 d 0.13 $/ton if $ST>$90 d
Landfill release	0.0588	11,782,000 $/release 26.2 $/ton	0.10	0.20	$60,000	3,000,000 $/claim 0.13 $/ton
Injection well release	0.0044	11,782,000 $/release 6.56 $/ton	0.10	0.20	$60,000	7,000,000 $/claim 0.02 $/ton
Accidental release during transport	Regional: 0.000042 Commercial: 0.00028	20,000 $/release 0.03-0.28 $/ton	0.10	0.20	$60,000	1,000,000 $/claim 0.52 - 4.63 $/ton
Release from operating facility	See Table 4.3					

Table 5.7: Natural resource damage expenses

	Zero estimate	Low estimate	Medium estimate	High estimate
$\wp(k_r)$	0.50	0.36	0.09	0.05
k_N ($/release)	0	$\leq 500{,}000$	500,000 - 5,000,000	$\geq 12{,}000{,}000$

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[22] The data represents average values taken from DOD (1987). Probability values are given on a yearly basis, and for the case of releases during transport they are given on a per trip basis. See Footnote 16 for comments regarding updating the tabulated figures.

Although it is quite difficult to estimate the less tangible benefits it is reasonable to assume that they may be significant (EPA, 1989). However, despite their significance no information is available in the literature to calculate these benefits and their particularity makes it difficult to develop a mathematical approach to estimate them. Moreover, like the previous cost category, calculating the less tangible benefits is judgmental in nature and the estimates obtained will contain a certain amount of uncertainty.

5.7 SUMMARY

This chapter presented the details of how to estimate the various costs and benefits associated with a given alternative. In summary, the main ideas to be taken out of this chapter include:

- As was outlined in the previous chapters, one of the most important advantages of applying waste minimization programs, is that of the potential economic benefits that can be obtained from their implementation. However, the identification of such benefits, both from a waste management and a regulation perspective is not so easily accomplished.
- The economic performance of the process will be measured —as discussed in Chapter 4— using the AEP. This economic tool considers the revenue obtained, as well as the usual costs, the direct costs, the hidden costs, the liability costs, and the less tangible benefits.

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[23] Drum releases are assumed not to result in compensation costs because they are expected to be cleaned up quickly before the contamination leaves the facility.

- Usual costs include the total fixed capital investment and the production costs generally associated with a process.
- Direct costs include the capital, operating, material, and maintenance costs involved in the treatment, recycling, handling, transportation, and disposal of waste. These costs will be estimated using Equation 5.4.
- Hidden costs include the expenses associated with permitting, monitoring, testing, training, inspection, and other regulatory requirements related to waste management practices. These costs that are generally not a direct function of the amount of waste generated, can be estimated using Equation 5.5 and the information given in Appendix B.
- Liability costs include the fines and penalties to be incurred when a facility is in non-compliance with the environmental regulations. In addition, these costs incorporate the future liabilities for remedial action, personal injury, and property damage associated with routine and accidental release of hazardous substances. The liability costs will be estimated using probability estimates to calculate their expected value using Equations 5.6 to 5.10 and Tables 5.5 to 5.7.
- Less tangible benefits include the benefits obtained as a result of the increase in revenues or decrease in expenses due to an improvement in consumer acceptance, employee relations, and corporate image. Despite their significance no information is available to calculate them making it difficult to develop a mathematical approach to estimate them.

CHAPTER 6

PROCESS OPTIMIZATION

The previous two chapters focused on the initial step within the alternative's evaluation phase. As can be seen in Figure 6.1, this chapter continues with this phase initiating the discussion of the optimization of process alternatives. This description in increasing order of complexity concludes with the method used to select the best source reduction alternative that maximizes the process' profit and minimizes its environmental impact under uncertainty.

6.1 INTRODUCTION

Optimization theory has seen applications in almost every field of science and the use of this concept can be found through out a wide range of publications. In a strict sense, optimization can be defined as "the maximizing or minimizing of a given function possibly subject to a set of constraints" (Parker, 1997, p. 174). That is, one is interested in finding the largest or smallest value assumed by a function. In this manner, process optimization techniques aid in the evaluation of process alternatives, and help the decision maker to identify the best option that can achieve a specific objective.

Process optimization techniques are traditionally applied based on a deterministic approach. That is, the output of the system can be predicted completely if its input and

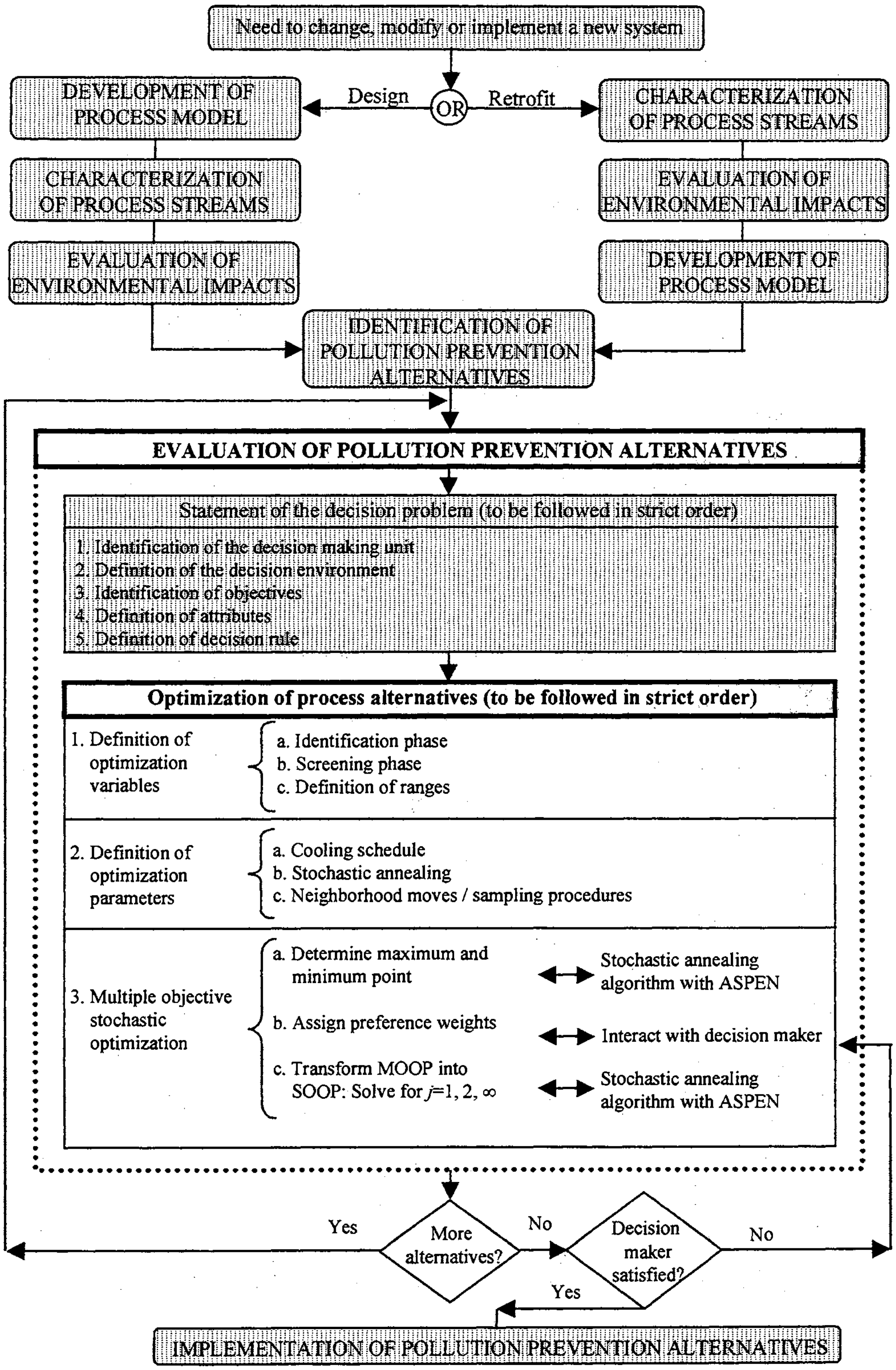

Figure 6.1: Road map[1] - Chapter 6

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[1] Lines/text in bold: topics discussed in this chapter. Shadow boxes: topics discussed in previous chapters.

initial state are known. Hence, for a particular state of the system, a given input always leads to the same output. Consequently, discrete optimization techniques are helpful in analyzing decisions made under complete certainty, and can be used to evaluate a single or a multiple objective optimization problem.

Stochastic optimization techniques represent a different approach in which "given the input and the state of the system, it is possible to predict only the range within which the output will fall and the frequency with which various particular outputs will be obtained over many repetitions of the observation" (Maisel and Gnugnoli, 1972, p. 13).

To understand the development of the final method proposed for evaluating source reduction alternatives under uncertainty, this chapter presents a review of optimization techniques for evaluating single and multiple objective problems. After a brief review of discrete optimization, including some useful definitions, the chapter focuses in the optimization of random or stochastic processes.

6.2 DISCRETE OPTIMIZATION WITH A SINGLE OBJECTIVE

The definition of optimization given earlier is helpful in identifying the main components of an optimization problem: the objective function to be maximized or minimized, and a set of equality and inequality constraints (see Equation 6.1)

Maximize or minimize

$$z = f(\mathbf{x},\mathbf{y}) \tag{6.1}$$

subject to

$$g(\mathbf{x},\mathbf{y}) = 0$$

$$h(\mathbf{x},\mathbf{y}) \leq 0$$

where:

z = objective function

$\mathbf{x}$ = vector of continuous variables

$\mathbf{y}$ = vector of integer variables

$g(\,)$ = set of equality constraints

$h(\,)$ = set of inequality constraints

The objective function in Equation 6.1 is used to represent the desired state of the system that the decision maker is trying to obtain and the values taken by this function are used to measure the objective's degree of achievement.

The set of constraints represent a group of equations that are used to describe in a mathematical form the behavior of the process. These equations are what constitute the process model that is used to evaluate and compare different investment options. For example, they may represent the mass and energy balances that must be satisfied for the model's validity. However, when dealing with process simulators, such as ASPEN PLUS™, most of these constraints are already internally specified.

In addition, the constraints may also define the problem's feasible solution region (see Figure 6.2). This region will enclose the attainable solutions that contain a set of variables, integer or continuous, that satisfy both the equality and inequality constraints.

Integer or discrete variables, as their name suggests, can take only integer values. In the case of process design, these variables are sometimes referred to as binary variables and are assigned a value of "0" or "1" to represent the presence or absence of a particular piece of equipment.

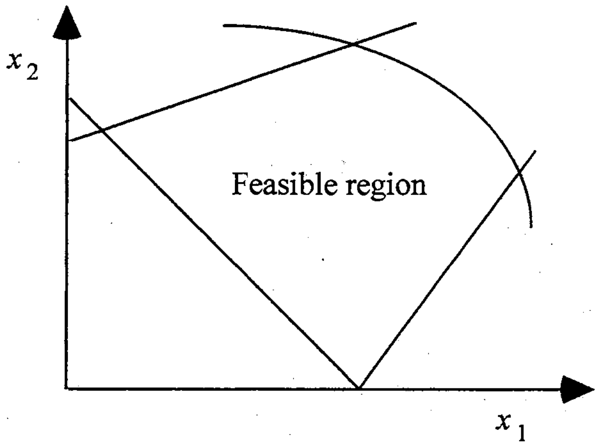

Figure 6.2: Feasible region for an optimization problem enclosed by inequality constraints

Continuous variables can take an infinite number of values within a given range. In the case of process evaluation studies, these variables (i.e., temperature, pressure, and flowrate) are used to denote possible changes in process operating conditions.

The complexity of the optimization problem in Equation 6.1 depends on the number of continuous and discrete variables. Therefore, a screening of these variables should be undertaken in order to determine those that have an important effect in the process performance, and those that have a small impact can be eliminated. A discussion of how this can be accomplished is given in Chapter 7.

Once the optimization problem has been defined, the next step is to choose the appropriate algorithm applicable to the problem's characteristics. To help the user decide which method to employ, various comparison studies have been published (Biegler and Hughes, 1983; Edgar and Himmelblau, 1988; Grossmann and Kravanja, 1995). However, regarding the optimization method selected, as Smith (1981) suggests, the limitations appear to reside not so much in which algorithm is used, but on the formulation of the objective function and the complete knowledge of the process.

6.3 DISCRETE OPIMIZATION WITH MULTIPLE OBJECTIVES

The preceding section dealt with optimization problems having only one objective. However, as has been previously discussed, there are some instances in which a single objective is not enough to describe the decision maker's desire state of the system. In this case, the optimization problem in Equation 6.1 is transformed into a multiple objective problem (see Equation 6.2).

Maximize or minimize

$$z_1 = f(\mathbf{x},\mathbf{y}),\ z_2 = f(\mathbf{x},\mathbf{y}),\ \ldots\ ,z_n = f(\mathbf{x},\mathbf{y}) \tag{6.2}$$

subject to

$$g(\mathbf{x},\mathbf{y}) = 0$$
$$h(\mathbf{x},\mathbf{y}) \leq 0$$

Multiple objective optimization is an approach that has been used to solve problems of the type given in Equation 6.2. There are several books and publications that present an overview of multiple criteria optimization theory, including Chankong and Haimes (1983), Cohon (1978), Goicoechea *et al.* (1982), Sawaragi *et al.* (1985), Stancu-Minasian (1990), Vanderpooten (1990) , and Yoon and Hwang (1995). In addition, a comprehensive bibliography on the subject is given by Stadler (1984). Several reviews have also been published that deal with specific applications. For example, engineering applications are reviewed by Goicoechea *et al.* (1982); chemical engineering applications by Clark and Westerberg (1983); management science applications by Anderson *et al.* (1991) and Kirkwood (1997); and environmental management applications by Munda *et al.* (1994) and Janssen (1992).

A multiobjective decision problem could in theory be solved using similar methods as those employed in solving a single objective optimization problem. However, in the case of multiple objective decisions the problem consists of a set of competing objectives. This implies that there is usually no alternative that maximizes or minimizes each criterion simultaneously. For example, in the present work, there is generally no investment option that maximizes the process' profit and minimizes its environmental impact. A sacrifice of the first objective is required to obtain a better performance of the second objective. As a consequence, the optimum solution obtained will be considered as the best compromise solution according to the decision maker's preference structure (Vanderpooten, 1990).

This compromise solution corresponds to a set of feasible answers, generally referred to as noninferior or Pareto optimal solutions. These solutions encompass the set of nondominated points that can become potential candidates for the best compromise criterion vector (see Definition 6.1)(Vanderpooten, 1990).

Definition 6.1: $z' \in \mathbf{Z}$ is nondominated iff there is no $z \in \mathbf{Z}$ such that $z > z'$.

That is, a nondominated point is one where any other point in the set of possible outcomes **Z**, which increases the value of one criterion also decreases the value of at least one other criterion. For example, in Figure 6.3 the line segments AB and BC correspond to the set of nondominated points for a two objective optimization problem where both

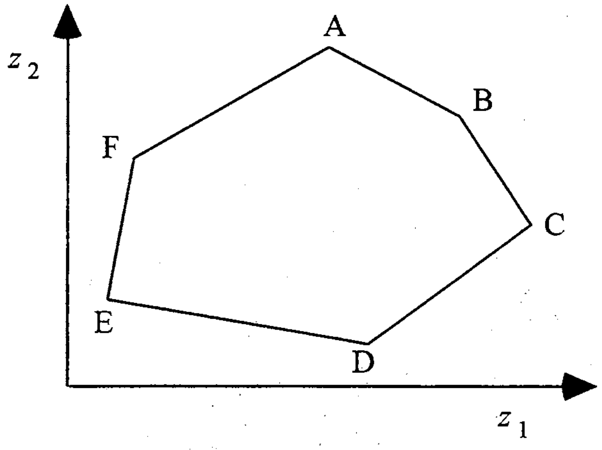

Figure 6.3: Nondominated points for a two objective optimization problem

objectives are to be maximized. In this case, if the solution obtained corresponds to point C, a sacrifice in z_1 is required to improve the performance of z_2.

The analytical methods for obtaining the best compromise solution can be classified in three general groups: (1) generating techniques, (2) techniques with prior articulation of preferences, and (3) methods of progressive articulation of preferences.

The generating techniques consist in finding an exact representation or at least an approximate one of the set of noninferior points. Once, this set has been determined it is presented to the decision maker in either graphical or tabular form. Consequently, the decision maker selects the best solution based on his specific preference structure.

The two remaining classifications, the techniques with prior articulation of preferences and the methods of progressive articulation of preferences, require decision makers to articulate their preferences and pass this information to the analyst. The main difference between them, is that the former requires the articulation of preferences in advance of the analysis; whereas, the latter involves a continuous interactive procedure between the analyst and the decision maker.

The main disadvantage of the generating techniques is that they are generally more computationally intensive than the preference oriented approaches. This is not surprising, since these techniques require the analyst to obtain the whole set of noninferior solutions, where each member of this set needs to be calculated using a mathematical programming method.[2]

The above discussion could favor the use of the preference oriented approaches. However, these too might be difficult to implement and may incur substantial costs in time and money to obtain. Nevertheless, the computational burden of the generating techniques —which as will be discussed later, increases as the process alternatives are evaluated under uncertainty— are the main reason for which this work incorporates preference oriented methodologies.

There are currently more than 20 methods within the preference oriented techniques and the question as to which approach to select is not so easily answered. For example, Gershon and Duckstein (1982) present an algorithm for choosing a multiobjective method. In their study, they develop a set of 28 criteria to evaluate a total of 13 methods. As can be seen in their study, and in other similar reviews such as MacCrimmon (1973), the technique selected will depend on the decision maker and on the problem's characteristics.

Within the category of prior articulation of preferences, probably the method used most in multiple criteria decision making is the goal programming approach proposed by Charnes and Cooper (1961). This technique identifies solutions that are closest to a

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[2] For example, if a process flowsheet is evaluated using a process simulator to determine the best temperature at which an equipment should be operated, the analyst would have to evaluate the flowsheet at each possible temperature and calculate its effect on the process' profit and environmental impact.

"specific goal" set by the decision maker determined by some measure of distance. However, in some instances targeting specific predetermined goals may lead to an inferior solution. For example, if in Figure 6.4 the decision maker has set G_1 and G_2 as the goals for z_1 and z_2, then the solution obtained would be inferior. And if the decision maker sticks with these goals, he would then have to settle for less than he should.

A similar approach to the goal programming technique that tries to avoid the caveat described in Figure 6.4, is the compromise programming tool (Zeleny, 1973; Zeleny, 1974; Zeleny, 1976) used in the proposed methodology. The compromise programming approach identifies solutions that are closest to the ideal solution as determined by some measure of distance (Goicoechea *et al.*, 1982). This method differs from the goal programming technique in that instead of measuring the closeness of the solution to a specific goal, it identifies solutions that are closest to an ideal point $\mathbf{z}^*$ that —as seen in Figure 6.4— is defined as the vector

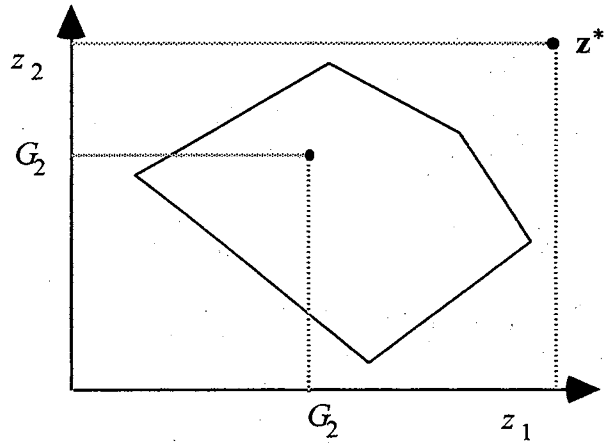

Figure 6.4: Comparison between goal programming and compromise programming

$$\mathbf{z}^* = \left(z_1^*, z_2^*, \ldots, z_n^*\right) \tag{6.3}$$

where:

$$z_i^* = \max z_i(\mathbf{x}, \mathbf{y})$$

The ideal solution in Equation 6.3 is generally not feasible. However, it can be used to evaluate the set of attainable nondominated solutions, by measuring its closeness to the nondominated solution (see Equation 6.4) (Goicoechea *et al.*, 1982).

$$L_j = \sum_{i=1}^{n} \gamma_i^j \left(z_i^* - z_i(\mathbf{x})\right)^j \tag{6.4}$$

where:

Lj = distance from the ideal point

γ = preference weight

j = compromise index, where $1 \le j \le \infty$

Consequently, a compromise solution with respect to j is defined as $\mathbf{x}_j{}^*$ such that

$$\min L_j(\mathbf{x}) = L_j\left(\mathbf{x}_j^*\right) \tag{6.5}$$

The preference weight in Equation 6.4 is used to represent the relative importance that each objective has to the decision maker. For example, suppose that the decision maker considers that it is two times more important to reduce z_1 than z_2. Hence, the analyst would assign a value of 2 to γ_1, while keeping $\gamma_2 = 1$.

The decision maker's preferences are also expressed in the compromise index, which represents his concern with respect to the maximal deviation (Goicoechea *et al.*, 1982). For example, if j=1, all deviations from the ideal point are weighted equal. In contrast, when j=2, each deviation is weighted in proportion to its magnitude. That is, the larger the deviation the larger the weight. This weight becomes larger as the compromise index is increased, until j=∞ when only the largest deviation counts. In this case, the best compromise solution is found by minimizing L_∞ (see Equation 6.6) (Cohon, 1978).

$$\min L_\infty = \max \gamma_i \left(z_i^* - z_i(\mathbf{x})\right) \tag{6.6}$$

As a result, the noninferior solutions defined within the range $1 \le j \le \infty$ correspond to the "compromise set" (in practice only three points of the compromise set are calculated: j=1, j=2, and j=∞) (Goicoechea *et al.*, 1982) from which the decision maker will still have to make the final choice in order to identify the best compromise solution. Nonetheless, this compromise set already includes some of the decision maker's preferences that were incorporated as weights.

<u>In summary, this study uses the compromise programming approach to evaluate source reduction alternatives under two competing objectives</u> (see Equation 6.7).

$$\min\ L_j = \gamma_{AEP}^j \left(\frac{AEP^* - AEP(\mathbf{x},\mathbf{y})}{AEP^* - AEP^{**}} \right)^j + \gamma_\theta^j \left(\frac{\theta(\mathbf{x},\mathbf{y}) - \theta^*}{\theta^{**} - \theta^*} \right)^j \tag{6.7}$$

subject to:

$$g(\mathbf{x},\mathbf{y}) = 0$$

$$h(\mathbf{x},\mathbf{y}) \le 0$$

where:

AEP = Annual equivalent profit

θ = Environmental impact

$AEP^{**} = \min\ AEP(\mathbf{x},\mathbf{y})$

$\theta^{**} = \max\ \theta(\mathbf{x},\mathbf{y})$

$AEP^{*} = \max\ AEP(\mathbf{x},\mathbf{y})$

$\theta^{*} = \min\ \theta(\mathbf{x},\mathbf{y})$

Equation 6.7 incorporates a scaling function to ensure that the objective functions are expressed in commensurable terms. In order to clarify this, consider that the AEP is measured in the thousands or even millions, whereas the environmental impact might be measured in the hundreds. This difference in scale, might consequently err in the identification of the compromise set.

6.4 STOCHASTIC OPTIMIZATION

The word stochastic comes from the Greek language and means random. Thereupon, a stochastic system can be defined as a collection of random variables that depend on a specific parameter, usually time. Where a random variable, can be thought of as a "discrete or continuous variable which can assume certain given values with definite probabilities." (Tintner and Sengupta, 1972, p.2).

The best way to understand the concept of a stochastic process is using a simple example. Lets suppose, a manufacturer is interested in measuring the cost of purchasing a given amount of raw materials over the next five years. In this case, the cost per year is given by multiplying the amount of raw material times its cost. However, even if the manufacturer has complete control over the amount required, he does not have any way of knowing the raw material's price. It might be possible only to get an estimate of the different prices and their corresponding probabilities. That is, the uncertainty in this parameter can be expressed in terms of probabilistic distributions that show the range of values the variable could assume and the likelihood of their occurrence. Hence, the uncertainty in this parameter transforms the simple process into a stochastic process.

The importance of considering uncertainty in a given scenario, has led to a comprehensive study and analysis of the behavior and theory behind stochastic processes in almost every scientific field[3]. A review on the subject is given by Ermoliev and Wets (1988), Kan and Stougie (1988), and Taylor and Karlin (1994). In addition, within chemical engineering stochastic models have been applied in process control (Carrasco and Banga, 1997), process synthesis (Acevedo and Pistikopoulos, 1998; Castell *et al.*, 1998; Chaudhuri and Diwekar, 1996; Chaudhuri and Diwekar, 1997; Dua and Pistikopoulos, 1998; Ierapetritou *et al.*, 1996), process modeling (Diwekar, 1999; Diwekar and Rubin, 1991), process planning (Ierapetritou *et al.*, 1996; Ierapetritou *et al.*, 1994; Liu and Sahindis, 1996), and analysis of process flexibility, reliability, and maintenance (Straub and Grossmann, 1993; Thomaidis and Pistikopoulos, 1995).

6.4.1 SINGLE OBJECTIVE STOCHASTIC OPTIMIZATION

The study of stochastic process has led to the development of stochastic optimization methods, in which Equation 6.1 is transformed into Equation 6.8.

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[3] For instance, a keyword search for the term "stochastic" identified more than 3,600 articles published on the subject between 1991 and 1996.

Maximize or minimize

$$z = f(\Omega, \mathbf{x}, \mathbf{y}) \tag{6.8}$$

subject to

$$g(\Omega, \mathbf{x}, \mathbf{y}) = 0$$

$$h(\Omega, \mathbf{x}, \mathbf{y}) \leq 0$$

where:

Ω = vector of uncertain parameters

That is, the solution to Equation 6.8 is given by the optimum values of the discrete and continuous variables, $\mathbf{y}^*$ and $\mathbf{x}^*$ respectively, that maximize or minimize the objective function z over all possible values taken by the uncertain parameters Ω.

A possible approach for solving the optimization problem in Equation 6.8, is to employ a scenario analysis. This method tries to solve the problem by finding the optimal solution for every possible value of Ω. However, as Ermoliev and Wets (1988) explain, it is not clear which is the final solution. To illustrate this, consider that the uncertain parameter can take only two values, then an optimum answer would be found for each of these values: $\mathbf{x}^1 = \mathbf{x}^*(\Omega^1)$ and $\mathbf{x}^2 = \mathbf{x}^*(\Omega^2)$. So the question still remains as to which of these two answers $\mathbf{x}^1$ or $\mathbf{x}^2$ corresponds to the true optimum. In other words, one cannot find a feasible solution vector $\mathbf{x}^1$ such that $f(\mathbf{x}^1, \Omega) \leq f(\mathbf{x}^2, \Omega)$ for every value of Ω and for every feasible x.

A more logical approach that is usually taken for solving Equation 6.8, is to replace the stochastic problem by a suitable deterministic problem (Stancu-Minasian, 1990). In this case, the problem is generally solved by finding the solution vectors **x***, **y*** that maximize or minimize the expected value of the objective function[4], subject to some a priori distribution of Ω. Hence Equation 6.8 can be rewritten as

Maximize or minimize

$$E(z) = f(\Omega, \mathbf{x}, \mathbf{y}) \tag{6.9}$$

subject to

$$g(\Omega, \mathbf{x}, \mathbf{y}) = 0$$

$$h(\Omega, \mathbf{x}, \mathbf{y}) \leq 0$$

where:

$E(z)$ = objective function's expected value

The expected value of the objective function in Equation 6.9 is obtained by finding its average value over all its possible values. However, as was discussed in Section 4.6 obtaining all these values is meaningless. Therefore, the approach usually taken is to take a sample of the objective function's distribution and calculate its average value using Equation 6.10.

$$\bar{z} = \frac{\sum_{i=1}^{ns} z_i}{n_s} \tag{6.10}$$

where:

$$z_i = f(\Omega, \mathbf{x}, \mathbf{y})$$

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[4] A summary of different ways of reformulating the stochastic problem in deterministic terms is given by Stancu-Minasian (1990). Some of the possible approaches include: maximization of the mean value, minimization of the variance, maximization of the mean value with a constraint on the variance, and maximization of the probability that the function exceeds a given level.

$\bar{z}$ = objective function's average value

n_S = sample size

The sample size in Equation 6.10 represents the number of samples taken from the uncertainty parameters distribution, and consequently the number of times the objective function needs to be evaluated. As the sample size increases, the average value of z in Equation 6.10 becomes more accurate. However, as n_S becomes larger, the number of times the objective function needs to be evaluated is incremented. This results in an augmentation in the problem's computational requirements. All in all, this computationally intensive sampling and evaluation process has been one of the problems associated with the application of stochastic optimization techniques.

Once the stochastic problem has been reformulated in a deterministic form, the problem in Equation 6.9 can be solved using discrete optimization methods. As was discussed earlier, the selection of the appropriate optimization algorithm depends upon the system's characteristics (e.g., the type of variables or the mathematical expressions). In the case of a chemical process, the model used to represent its behavior is usually constructed in terms of nonlinear equations. In addition, in some cases such as process design or retrofit studies, the problem incorporates a vector of integer variables that denote the existence of a piece of equipment. Consequently, the problem to be solved can be classified as a mixed integer non linear programming (MINLP) problem.

Traditional MINLP methods —such as the branch and bound, generalized Benders decomposition, and outer approximation algorithms— have been successfully applied in the case of process synthesis applications. For example, Kravanja and

Grossmann (1995) present a review of these applications and give a brief description and further references for the main MINLP methods.

In spite of their success, the traditional MINLP approaches to synthesis may pose certain problems especially with sequential process simulators, such as ASPEN PLUS™ (Chaudhuri and Diwekar, 1997; Dantus, 1995). In addition, the presence of integer variables results in an increase in the computational complexity of the problem and can provoke further discontinues in the process model. Furthermore, by definition the traditional MINLP methods —that employ optimization subroutines such as successive quadratic programming (SQP)— terminate in a local minimum that depends on the initial configuration for which no guidelines are available to select it (van Laarhoven and Aarts, 1987).

An alternative approach that circumvents the problems associated with the traditional MINLP algorithms is the use of random search methods. Among the different random approaches used in process optimization —such as the extension-rotation algorithm, the sampling and clustering algorithm, the Bayesian testing algorithm (Maffioli, 1987)— the method that has probably received the most attention is the simulated annealing algorithm[5]. The simulated annealing algorithm does not depend on the initial guess and has the feature of exploring more globally the feasibility region of a given problem, thus having a good probability of finding the global optimum (van Laarhoven and Aarts, 1987).

The simulated annealing algorithm was initially proposed by Kirpatrick *et al.* (1983) to calculate an approximate solution for large combinatorial problems —such as

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[5] A comparison study of different random optimization methods is given by Brooks and Verdini (1988).

the classic traveling salesman dilemma[6]—, involved in the optimization of integer problems (a comprehensive theoretical analysis of this algorithm is given by Aarts, 1989; Bohachevsky *et al.*, 1995; Kirpatrick *et al.*, 1983; and van Laarhoven and Aarts, 1987). The method was later extended by Bohachevsky *et al.* (1986) and Vanderbilt and Louie (1984) to include the handling of continuous variables.

Taking into account its original purpose, it follows that since its development the simulated annealing algorithm has been applied in the solution of various kind of problems within a wide range of disciplines. For instance, Collins *et al.* (1988) present a bibliography review on different application areas, such as biology, physics, chemistry, computer design, and statistics. In addition, within chemical engineering, the simulated annealing algorithm has been applied in the analysis and design of chemical processes (Cardoso *et al.*, 1997; Dolan *et al.*, 1989; Floquet *et al.*, 1994; Kalivas, 1995; Ku and Karimi, 1991; Li *et al.*, 1999).

The simulated annealing algorithm is based on the analogy between the simulation of the annealing of solids and the solving of large combinatorial optimization problems. Within the area of physics, annealing denotes a physical process in which a solid is heated up by increasing the temperature of a heat bath. The temperature is raised until a maximum value is reached at which all particles of the solid randomly arrange themselves in the liquid phase. The process continues with a cooling phase where the temperature of the heat bath is lowered slowly. In this way, all particles arrange themselves in the low energy ground state, provided that the maximum temperature is

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[6] Given a list of *N* cities and the cost of traveling between each one, the traveling salesman problem consists in finding the optimal salesman's route, which will pass through each city once and return to the initial starting point, while minimizing the cost.

sufficiently high and the cooling is carried out sufficiently slow (van Laarhoven and Aarts, 1987).

At each temperature, as the solid is being cooled, the system is allowed to reach thermal equilibrium. In this equilibrium, the probability of being in a given state *i* with energy E_i is given by the Boltzmann distribution (see Equation 6.11).

$$\wp(\text{state} = i) = \frac{1}{Z(T)} \cdot \exp\left(-\frac{E_i}{k_B T} \right) \tag{6.11}$$

where:

E = energy

$Z(T)$ = partition function

k_B = Boltzmann constant

T = temperature

As the temperature decreases, the Boltzmann distribution concentrates on the lower energy states, and when the temperature approaches zero, only the minimum-energy states have a non-zero probability of occurrence. However, if the system is cooled too fast, the solid is not able to reach thermal equilibrium, resulting in metastable amorphous structures instead of the desired low-energy crystalline structure (Aarts and van Laarhoven, 1989).

To simulate the system's evolution to thermal equilibrium Metropolis *et al.* (1953) proposed a Monte Carlo method, known as the Metropolis algorithm (see Table 6.1), that is used to provide an efficient simulation of a collection of atoms in equilibrium at a given state. By repeating the procedure in Table 6.1 many times, one is able to

Table 6.1: Metropolis algorithm (Rowley, 1994)

Step 1:	Establish an initial configuration
Step 2:	Make a random trial change
Step 3:	Compute ΔE, the change in energy of the system due to the trial change
Step 4:	If $\Delta E \leq 0$ accept the new configuration
Step 5:	If $\Delta E > 0$ accept the new configuration with a probability $\exp(-\Delta E/T)$. In other words, generate a random number r, and when $\exp(-\Delta E/T) \geq r$, accept the configuration. Otherwise if $\exp(-\Delta E/T) < r$ retain the previous configuration.
Step 6:	Repeat the moves over a sufficient number of trials

simulate the thermal motion of atoms in thermal contact with the heat bath at a temperature T (Kirkpatrick *et al.*, 1983).

The Metropolis algorithm is useful as the analogy is made between the physical annealing process and the solving of optimization problems. In the case of the latter, the energy term is replaced by the objective function and the Metropolis algorithm is used to generate a population of configurations for a specific optimization problem at some given temperature. This "temperature" is used simply as a control parameter.

The simulated annealing algorithm —as the physical annealing process— initiates at a high "temperature", and it is cooled until it reaches a point where no further changes occur. At each "temperature", sufficient configuration changes are made until the system reaches equilibrium. From an optimization point of view, the simulated annealing algorithm is a random search method in which the configuration of the various variables are accepted if they result in a reduction in the objective's function value, and in the case of resulting in an increase they are accepted with a certain probability. Initially, when one is far away from the optimum point, the algorithm accepts more uphill moves, but — according to the Metropolis algorithm— as it approaches the optimum, less uphill moves are accepted.

The possibility of accepting uphill moves is one of the method's main advantage, since it prevents the algorithm from being trapped in a specific neighborhood or local optima. In addition, as Bohachevsky *et al.* (1995) explains, the method is also applicable to nonconvex objective functions with multiple optima and to discontinuous functions; as well as being useful for the optimization of either discrete or continuos variables.

In spite of these advantages, the algorithm's main criticism is its high computational requirements due to the large amount of trials that need to be evaluated. The number of configurations to be analyzed depend, first of all, on the specific algorithm's parameters; such as the initial "temperature", a rule for changing the current value of the control parameter, the equilibrium criteria, and the final "temperature" or stopping criterion. The selection of these parameters, also known as "cooling schedules", is a critical step in the algorithm's implementation[7]. And to aid in its selection, a review of different possible cooling schedules is given by van Laarhoven and Aarts (1987) and Collins *et al.* (1988).

Apart from the careful selection of the algorithm's main parameters, other authors have suggested different modifications in the method's structure and design features aimed at reducing the number of iterations by enhancing the algorithms performance (e.g., Andricioaei and Straub, 1996; Rakic *et al.*, 1995; Painton and Diwekar, 1995; Tovey, 1988; Yamane *et al.*, 1998; and Collins *et al.*, 1988).

An interesting approach —to be used in the present work— is the one given by Painton and Diwekar (1995), who developed a modified algorithm referred to as the "stochastic annealing algorithm," that has proven to be more efficient in finding the optimal solution (Chaudhuri and Diwekar, 1996). The main purpose of this new algorithm is to include a function that penalizes the objective function, in such a manner that the error incurred in sampling the objective function's distribution —for example due to a small sample size— is accounted for. In addition, through a weighting function, the algorithm considers that at high temperatures it is not necessary to take large samples since it is exploring the solution space; however, as the system gets cooler more information is needed so as to obtain a more accurate value of the objective function. Hence, this weighting function increases the size of the penalty as the temperature level rises.

To accomplish these effects, Painton and Diwekar (1995) include a penalty function as part of the objective function (see Equation 6.12)

$$E(z) = \frac{\sum_{i=1}^{n_s} z_i}{n_s} + b(T_L)\frac{2\sigma}{\sqrt{n_s}} \tag{6.12}$$

where:

$b(T_L)$ = weighting function

σ = objective function's standard deviation = $\sqrt{\frac{\sum_{i=1}^{n_s}(z_i - \bar{z})^2}{n_s - 1}}$

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[7] A detailed discussion on the selection of these parameters is given in Chapter 7.

The penalty function —the second term in Equation 6.12— consists of two parts: the error bandwidth $2\sigma/\sqrt{n_s}$ and the weighting function *b(t)*. The former corresponds to the error associated with estimating the actual mean of the objective's function distribution. Hence, as the number of samples taken increases, the error is reduced and the penalty is minimized.[8]

The weighting function, the penalty function's second part, as explained earlier allows the algorithm to increase the number of samples as the optimum point is being approached, augmenting the size of the penalty as the temperature level rises (see Equation 6.13)

$$b(T_L) = \frac{b_0}{k^{T_L}} \tag{6.13}$$

where:

b_0 = weighting function constant, usually small (i.e., 0.001)

k = constant that governs the rate of increase

T_L = temperature level

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[8] The error term in Equation 6.12 represents the width of the interval in the estimate of the population's mean. In statistical inference applications, this estimate is given by

$$\bar{x} \pm c\,\sigma/\sqrt{n_s}$$

where c depends upon the degree of confidence that all the samples taken will produce the interval that contains the population mean μ. In their algorithm, Painton and Diwekar (1995) consider only the upper bound of the 95% confidence interval. In this case, c is approximately equal to 2, and the error becomes

$$2\sigma/\sqrt{n_s}$$

For a further review on the subject of statistical inference, see the books by Bethea *et al.* (1975) and by Pfaffenberger and Patterson (1987), as well as the discussion given by Painton and Diwekar (1995).

In addition, at each iteration, the stochastic annealing algorithm updates the number of samples to be taken using the following relationship[9] (see Equation set 6.14) (Chaudhuri and Diwekar, 1996)

If $rand[0,1] \leq 0.5$ then

$$n_s = n_s + S_s \cdot rand[0,1]$$

otherwise,

$$n_s = n_s - S_s \cdot rand[0,1] \tag{6.14}$$

where:

S_S = number of samples step size

$rand[0,1]$ = uniform random number between 0 and 1

In summary, up to this point it should be clear that this work combines the compromise programming (CP) approach and the stochastic annealing (SA) algorithm to analyze source reduction alternatives under uncertainty using two competing objectives. Therefore, before concluding this chapter, the next section discusses how these two approaches —CP and SA — are combined to evaluate waste minimization projects.

6.4.2 MULTIPLE OBJECTIVE STOCHASTIC OPTIMIZATION

The discussion presented in this chapter has with increasing complexity dealt with the solution of various kinds of optimization problems. This discussion, is helpful in

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[9] To comprehend how updating the number of samples taken affects the penalty term and consequently the objective function in Equation 6.12, consider that for example two configurations are being evaluate. The expected value of these configurations was obtained using a sample size of 5 and 20 respectively. Lets further suppose that the average value of z calculated was 30 for both configurations. Hence, during the first temperature levels the penalty term is almost insignificant. However, as the temperature level is increased so does the importance given to the sample size. For example at $T_L = 70$, $E(z) = 30+7.1$ for $n_s=5$ and $E(z) = 30+3.5$ for $n_s=20$. Therefore, the algorithm — for a minimization problem— will choose the lesser of 33.5 that has a larger sample size and consequently is a better representation of $E(z)$.

understanding why, as Stancu-Minasian (1990:73) explains, "in solving the stochastic programming problems with multiple objective functions one is confronted with almost intractable difficulties and ambiguities."

In the present work, the solution to the multiobjective stochastic optimization problem in Equation 6.15

Maximize or minimize

$$z_1 = f(\Omega,\mathbf{x},\mathbf{y}),\ z_2 = f(\Omega,\mathbf{x},\mathbf{y}),\ \ldots,z_n = f(\Omega,\mathbf{x},\mathbf{y}) \qquad (6.15)$$

subject to

$$g(\Omega,\mathbf{x},\mathbf{y}) = 0$$

$$h(\Omega,\mathbf{x},\mathbf{y}) \leq 0$$

will be obtained combining the compromise programming approach and the stochastic annealing algorithm (see Equation 6.16).

$$\min\ E(L_j) = \gamma^j_{AEP}\left(\frac{E(AEP^*) - E(AEP)}{E(AEP^*) - E(AEP^{**})}\right)^j + \gamma^j_{\theta}\left(\frac{E(\theta) - E(\theta^*)}{E(\theta^{**}) - E(\theta^*)}\right)^j \qquad (6.16)$$

Equation 6.16, corresponds to the mathematical expression that will be used to evaluate the possibility of implementing source reduction alternatives. The details of how this will be accomplished using the process simulator ASPEN PLUS™ is presented in the next chapter.

Lastly, it should be pointed out that the solutions obtained using Equation 6.16 defined within the range $1 \leq j \leq \infty$ correspond to the "compromise set", from which the decision maker will still have to make the final choice to identify the best compromise solution.

6.5 SUMMARY

This chapter presented the theoretical background leading to the identification of the algorithm that will be used to evaluate waste minimization projects under a multiple objective stochastic optimization approach. The details of how this algorithm can be applied using the process simulator ASPEN PLUS™ are given in the next chapter. In summary, the main ideas to be taken out of this chapter include:

- Multiple objective optimization techniques will be used to analyze process alternatives under two competing objectives: maximize AEP and minimize the environmental impact.
- Among the various methods available for multiple criteria decision making, this work incorporates the use of a preference oriented approach: the compromise programming tool.
- Stochastic optimization techniques consider the analysis of stochastic systems that given its input and state, it is possible to predict only the range within which the output will fall and the frequency with which various particular outputs will be obtained.
- Among the various stochastic optimization methods, the present work incorporates the simulated annealing algorithm. This method does not depend on the initial guess and has a good probability of finding the global optimum. In addition, it is applicable to nonconvex objective functions with multiple

optima and to discontinuous functions; as well as for the optimization of discrete or continuos variables.

- Several modifications to the algorithm have been proposed to improve its performance. Among them, this work incorporates the "stochastic annealing algorithm".

CHAPTER 7

MULTIPLE OBJECTIVE STOCHASTIC OPTIMIZATION

The previous chapter discussed the mathematical approaches used to evaluate source reduction projects using multiple objective stochastic optimization (MOSO) techniques. As can be seen in Figure 7.1, this chapter continues with this discussion presenting the details of how to solve MOSO problems using the process simulator ASPEN PLUS™ (version 9.3-1).

7.1 INTRODUCTION

The proposed methodology for the implementation of waste minimization programs, as previously discussed in Chapter 3, consists of six steps: characterization of process streams, evaluation of environmental impacts, development of process model, identification of pollution prevention alternatives, evaluation of pollution prevention alternatives, and implementation of pollution prevention alternatives.

The evaluation of alternatives has been discussed in detail in the last three chapters. Continuing with this discussion, this chapter concludes the description of this phase by outlining the procedure to solve MOSO problems using ASPEN PLUS™, once the uncertain parameters and the optimization variables and parameters have been specified.

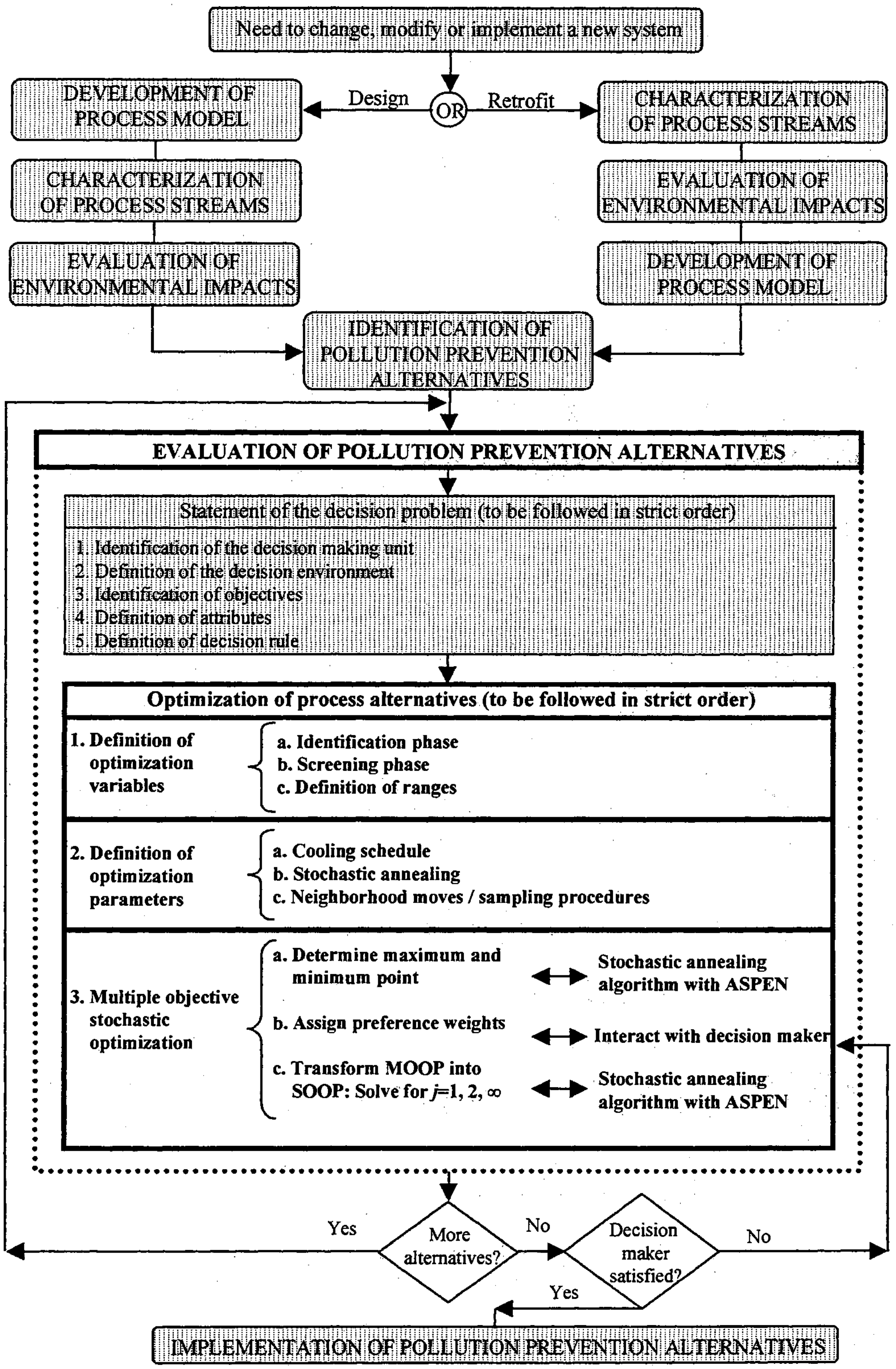

Figure 7.1: Road map[1] - Chapter 7

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[1] Lines/text in bold: topics discussed in this chapter. Shadow boxes: topics discussed in previous chapters.

7.2 DEFINITION OF OPTIMIZATION VARIABLES AND UNCERTAIN PARAMETERS

The number of variables included in the optimization study, as well as the number of uncertain parameters can become a key factor in the complexity of the evaluation of source reduction alternatives. Therefore, a selection should be made as to which of these variables or parameters have an important effect in the process' performance. This is accomplished through a three step procedure: (1) identification phase, (2) screening phase, and (3) definition of ranges phase.

7.2.1 IDENTIFICATION PHASE

The identification phase consists in the listing of all the possible discrete and continuous variables, as well as the uncertain parameters. The discrete variables include all the "new" units or pieces of equipment that have been suggested generally in the identification of pollution prevention alternatives phase (see Section 3.5).

The continuous variables are normally associated with the process operating conditions. In addition, they include all those variables that are related to the performance of the new units. In identifying these parameters, apart from the techniques described in Section 3.5 it might be helpful to construct a cause-effect diagram (see Figures 7.2 and 7.3), that has been widely used as a tool to identify the different factors that can affect the performance of a given system.

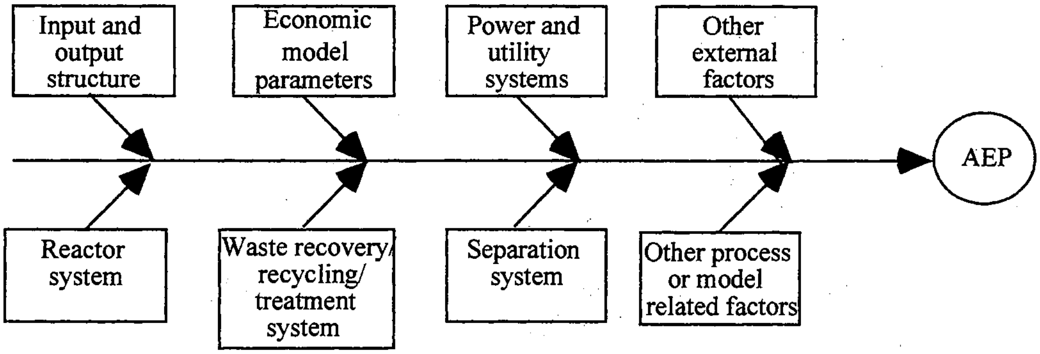


Figure 7.2: Annual equivalent profit cause-effect diagram

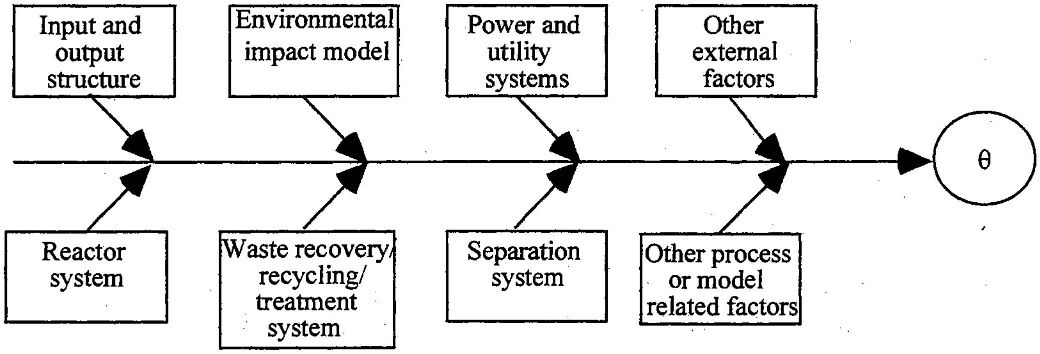


Figure 7.3: Environmental impact cause-effect diagram

The uncertain parameters, of which some information is known or can be assumed, are the ones responsible for the riskiness in the evaluation of investment projects. These parameters can be also be identified using Figures 7.2 and 7.3.

7.2.2 SCREENING PHASE

Once the variables and parameters have been identified, their screening can be done using experimental design techniques, of which a review on the subject can be found in Box *et al.* (1978), Juran (1974), and Ross (1996). In these techniques, a small group of experiments is used to obtain information about the effect of each variable or parameter, as well as the possible interaction between them. Assuming a two level experimental design, in which variables are evaluated at a lower value (-) and at an upper value (+), the number of experiments is given by 2^k, where k corresponds to the number of variables under study.

Depending upon the information required, a fraction of the factorial design can be employed, in such a manner as to reduce the number of experiments, for example 2^{k-1} or 2^{k-2}. However, as this number is reduced, a sacrifice is made on the accuracy, quality, and amount of information obtainable. Nevertheless, one of the main advantages of the fractional factorial designs, is that it is not required to evaluate all possible variable combinations. Hence, being useful in implementing screening studies. Therefore, the the screening of optimization variables and uncertain parameters will be carried out using experimental design techniques as described in Table 7.1 (see Appendix C).

Table 7.1: Screening of variables and parameters using experimental design techniques

1. The lower and upper values of each variable and parameter are specified. For the discrete variables, these values correspond to " 0" and " 1" respectively. For continuous variables, levels can be set based on physical or process constraints; or an alternative option is to fix the upper and lower levels, for example to ±10% of the base case value. This simple rule can also be used for the uncertain parameters, for which in some instances a best case-worst case scenario could be more appropriate.

2. Based on the degree of resolution required and the number of variables, a design matrix is constructed (Box *et al.*, 1978; Ross, 1996).

Experiment No.	x_1	x_2	…	x_k
1	–	–		–
2	+	–		–
⋮				
n	+	+		+

3. Each experiment is carried out by setting the variables at their corresponding upper and lower values, and recording the AEP and environmental impact calculated. When using ASPEN PLUS™ this can be done easily using the case study tool.

4. The results obtained through the experimentation process are used to calculate the various effects with the aid of a contrast coefficient table (Box *et al.*, 1978).

7.2.3 DEFINITION OF RANGES

The definition of the ranges phase involves the specification of the optimization limits for the variables identified in the screening phase. For the discrete and continuous variables the ranges can be estimated as was done in the experimental design analysis (see Table 7.1). For the case of the uncertain parameters their variability can be expressed in terms of probabilistic distributions that show the range of values the parameter could take and the likelihood of occurrence of each value within that range. Depending on their characteristics, there are different distributions to express the process variability. In risk simulation, some of the most frequently used distributions are the uniform, normal, triangular, lognormal, and beta distributions (Park and Sharp-Bette, 1990) (see Table 7.2 and Figures 7.4 to 7.7).

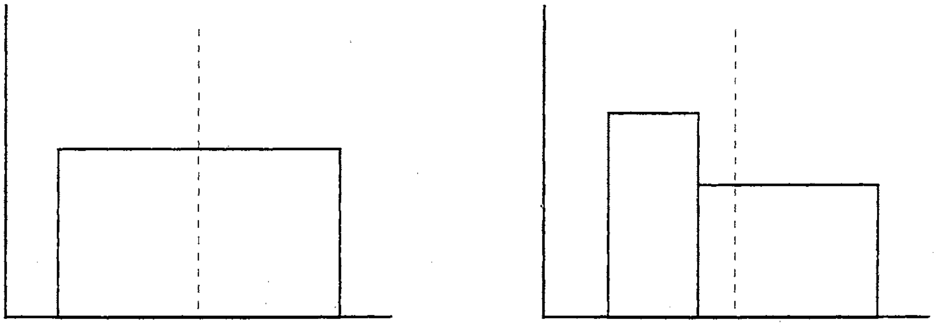
7.3 DEFINITION OF STOCHASTIC ANNEALING PARAMETERS

The analysis of investment alternatives, as discussed in Chapter 6, will be done combining the compromise programming approach and the stochastic annealing algorithm. However, before the latter can be applied several key parameters need to be specified, in order to ensure a good performance of the algorithm. As described in the next sections, the appropriate choice of these parameters will not only reduce the amount of iterations required, but will also guarantee that a global optimum has been obtained.

As was shown in Figure 7.1, three sets of parameters are required for the correct definition of the stochastic annealing algorithm: (1) the cooling schedule, that considers the choice of the simulated annealing parameters, (2) the stochastic annealing set, that

Table 7.2: Distribution types

Distribution type	Description
Uniform (Figure 7.4)	Assumes that all possible values that the uncertain parameter can take are equally likely. This distribution is widely used in process simulation applications since random variates from other distributions can be generated from a uniform distributed variable using specific transformation techniques. A review of such techniques is given by Banks and Carson (1984), Law and Kelton (1984), and Park and Sharp-Bette (1990).
Normal or Gaussian (Figure 7.5)	Is probably the most important and the most used probability distribution and it reflects a symmetric but varying probability of a parameter value being above or below the mean value.
Lognormal (Figure 7.6)	Are skewed in such a way that there exists a higher probability of a value falling on one side of the median than the other (Diwekar and Rubin, 1991).
Triangular (Figure 7.6)	Are skewed in such a way that there exists a higher probability of a value falling on one side of the median than the other (Diwekar and Rubin, 1991).
Beta (Figure 7.7)	Is very flexible in representing the variability of a process variable, and once its parameters are specified it can take a wide range of shapes. For example, it can be used to represent an optimistic estimate, a pessimistic estimate, and a most likely estimate (Park and Sharp-Bette, 1990).
User specified	Can be used to represent any arbitrary characterization of uncertainty, including fixed probabilities of discrete variables (Diwekar and Rubin, 1991). The latter application can be used in the case where if for instance some event occurs, the parameter will take on a specific value. To put in another way, suppose that a parameter is defined using the following relationships: If rand(0,1) < 0.8 then $\Omega = 5$ and If rand(0,1) > 0.8 then $\Omega = 10$ Hence in this example, the uncertain parameter has an 80% probability of taking the value of 5 and a 20% probability of doubling its response. That is, once a random number is generated its value will determine the uncertain parameter response.



(a) (b)

Figure 7.4: (a) Uniform distribution and (b) modified uniform distribution

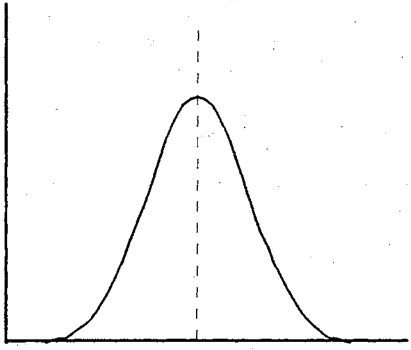


Figure 7.5: Normal distribution

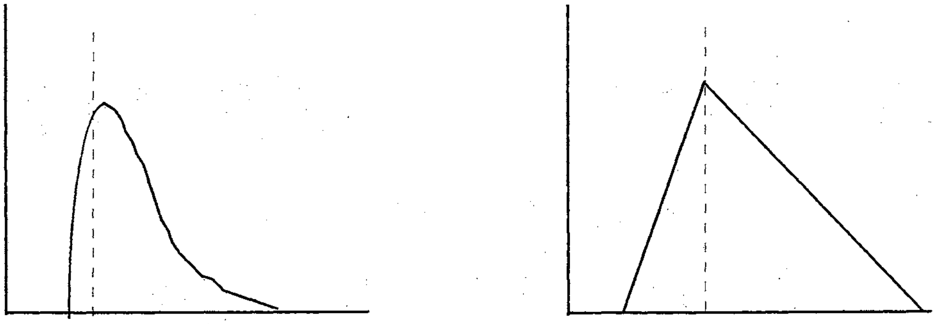


Figure 7.6: Lognormal and triangular distributions

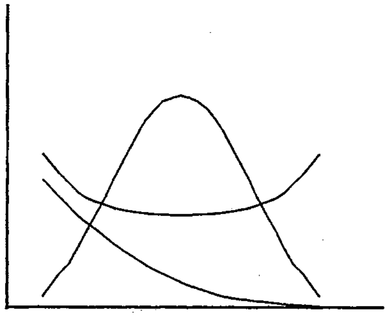


Figure 7.7: Beta distribution

includes the weighting function's parameters and sample size information, and (3) the specification of the neighborhood moves and sampling procedures.

The next sections describe the definition of each one of these set of parameters. However, in order to clarify the discussion, the reactor used in the manufacture of methyl chloride[2] through the thermal chlorination of methane (see Figure 7.8) is used as a simple example where the purpose is to maximize the potential cash input that can be obtained from the selling of the process' main product, methyl chloride. In this case, the problem consists of two continuous variables: the reactor temperature and the chlorine flowrate; and one uncertain parameter: the methyl chloride selling price.

7.3.1 COOLING SCHEDULE

The successful implementation of the simulated annealing algorithm requires the specification of four parameters: (1) the initial value of the temperature —the control parameter—; (2) the final value of the temperature or stopping criterion; (3) a rule for

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[2] The manufacture of methyl chloride is used only as a brief example to clarify the use of experimental design techniques. This process is also used as an example throughout the end of the chapter. Since the production of methyl chloride is discussed in detail in the next chapter, only a brief mention of it is included in the present section.

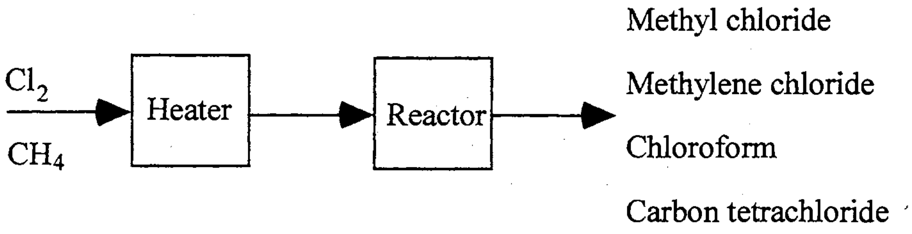

Figure 7.8: Reactor system for the manufacture of methyl chloride

changing the current value of the control parameter; and (4) the equilibrium criteria, that is the number of trials at a given temperature or what is referred to as the length of the Markov chain[3]. A selection of these parameters, as well as their combination is also known as the "cooling schedule," and it is considered a critical step in the algorithm's application. Hence, the search for adequate cooling schedules has been addressed in many publications (e.g., Bohachevsky *et al.*, 1995; Collins *et al.*, 1988; and van Laarhoven and Aarts, 1987). Yet, the cooling schedule selected will depend upon the problem's characteristics and the analyst's preferences.

Initial value of the temperature (control parameter)

The simulated annealing optimization algorithm initiates at a high "temperature" and it is cooled until it reaches a point where no further changes occur. At each temperature level, sufficient neighborhood moves are made until the system reaches equilibrium. Hence, within the algorithm's design the temperature is used mainly as a

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[3] A Markov chain can be described as a series of random events, where the probability of occurrence of each event depends only on the preceding outcome (Parker, 1997). That is the new configuration will depend only on the present one.

control parameter and as its value is decreased and reaches a freezing point, the system approaches an optimum point (see Figure 7.9).

The initial temperature selected has an important effect on the number of neighborhood moves and consequently on the number of times the objective function is evaluated. For example, in Figure 7.9 with an initial temperature T_0 of 100, almost 73,000 flowsheet passes were required to find the optimum point. However, if the initial temperature is lowered to 50 only 25,000 flowsheet evaluations are needed. A further reduction of T_0 to 25 leads to a similar[4] optimum point with only 16,700 iterations[5]. This implies that if very high temperatures are selected the algorithm may spend too much time exploring the search region and unnecessarily waste computer time. Hence, one would be inclined to choose the smallest possible value as an initial value for the control parameter. However, by doing so the algorithm could then be trapped in a local optima.

The initial value for the control parameter is usually selected such that the acceptance ratio ξ (number of transitions accepted / number of proposed transitions) is approximately equal or greater than a given number close to 1. For example, Aarts and van Laarhoven (1989) suggest that ξ=0.95, Painton and Diwekar (1995) use a value of 0.98, whereas Kirkpatrick *et al.* (1982) suggest in their original report an acceptance ratio of 0.8 (van Laarhoven and Aarts, 1987). This value of 0.8 is part of a simple rule, to be used in this work, in which an initial Markov chain is evaluated, and if ξ<0.8 the initial temperature is doubled. This procedure is then continued until ξ>0.8.

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[4] The different parameter studies may lead only to "similar answers", since due to the stochastic nature of the process, no two responses found will be equal.

[5] The term iteration used throughout this chapter and the remaining chapters refers to a completely converged flowsheet evaluation.

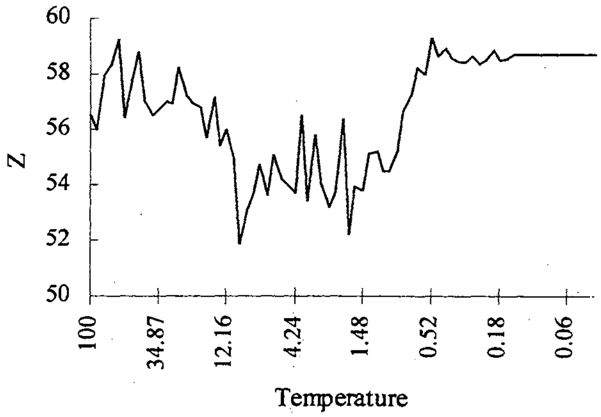

Figure 7.9: Optimization of methyl chloride reactor system

Stopping criteria

The stopping criteria will determine the final value of the control parameter. As van Laarhoven and Aarts (1987, p.58) explain "a stop criterion is usually based on the argument that execution of the algorithm can be terminated if the improvement in cost, to be expected in the case of continuing execution of the algorithm, is small."

Referring to the physical annealing process, the stopping criterion is in general known as the freezing temperature. Hence, this criterion can be determined by setting the final temperature to a fixed value. Other possible approaches include establishing the number of times the algorithm needs to be executed (Bonomi and Lutton, 1984) (however it is not clear how this number should be determined), terminating the algorithm if only a small change in the objective function is detected in the last successive changes (Aarts and van Laarhoven, 1989; Bohachevsky *et al.*, 1995), or by terminating the algorithm if the last configurations of a certain number of consecutive Markov chains have remained unchanged (Kirkpatrick, et al., 1983). This work incorporates a combination of the last two approaches stopping the algorithm's execution when the change in the last five consecutive Markov chains is less that a specified tolerance.

Temperature function

The temperature function represents the rule for changing the current value of the control parameter. Before this rule is chosen, one should return to the definition of the physical annealing process in which if the system is cooled too fast the desired low-energy crystalline structure will not be obtained. For example, consider one of the simplest temperature functions (see Equation 7.4).

$$T_{i+1} = \alpha_T T_i \tag{7.4}$$

where:

α_T = temperature function constant

Values for α_T can range between 0.5 to 0.99 (van Laarhoven and Aarts, 1987); and as its value is reduced so is the number of temperature levels that are evaluated, and consequently the number of iterations required. However, using such a small value as 0.5 can lead to an erroneous algorithm performance (see Figure 7.10).

Apart from Equation 7.4, different functions have been proposed ranging from simple ones to complex relationships. That for example are dependent on the algorithm's evolution. A review of these relationships is given by Collins *et al.* (1988) and van Laarhoven and Aarts (1987). In this work, due to its simplicity the temperature

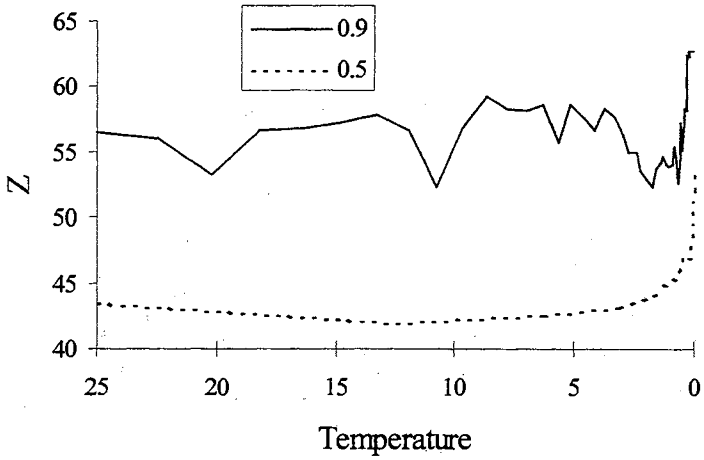

Figure 7.10: Effect of the temperature function constant[6]

function employed will be the one given in Equation 7.4, where the temperature function constant was set to 0.9.

Markov chain length

The neighborhood moves, as explained in Chapter 4, need to be classified as Markov chains for the algorithm to attain a global optimum. The length of these chains is related to the number of neighborhood moves to be evaluated before the system is said to have reached equilibrium. And, as can be observed this parameter and the selection of the temperature function are interrelated, and their combination can greatly affect the algorithm's performance.

The simplest choice is to set the length of the Markov chain M_L to a fixed value (Bonomi and Lutton, 1984). This approach could seem appealing, but in this case the

---

[6] The number of iterations required for generating the data in Figure 5.10 was of approximately 10,800 and 16,150 for α_T equals 0.5 and 0.9 respectively.

number of moves is independent of the algorithm's performance at a given temperature level. This makes it difficult to set an initial Markov chain length that would be applicable throughout the optimization problem. Other alternative approaches include to continue at the current temperature level until the change in the objective function is small. In addition, several mathematical expressions have been proposed to determine the Markov chain length primarily as a function of temperature (Collins *et al.*, 1988).

A common choice is to continue evaluating neighborhood moves until a specific minimum number of transitions has been accepted. A caveat usually associated with this method is that as the temperature is decreased fewer number of transitions are accepted until a point is reached where as $T \rightarrow 0$, $M_L \rightarrow \infty$. Therefore, a limit is usually placed on the maximum number of configurations $M_L^{\max}$ to evaluate at each temperature level. For example, Kirkpatrick *et al.* (1982) propose that $M_L^{\max} = n$ (van Laarhoven and Aarts, 1987), where n is the number of variables; Vanderbilt and Louie (1983) set $M_L^{\max} = 15n$; and Bohachevsky *et al.* (1995) uses up to 7500 trial moves per level for a two variable optimization problem.

The present research incorporates the last approach described where at a given level the algorithm continues evaluating configurations until 10 transitions have been accepted or until a maximum of 10n neighborhood moves have been made.

7.3.2 STOCHASTIC ANNEALING PARAMETERS

The stochastic annealing algorithm, in addition to the parameters described in the previous section, requires the specification of the weighting function (see Equation 7.5)

$$b(T_L) = \frac{b_0}{k^{T_L}} \tag{7.5}$$

The weighting function constant b_0 in Equation 7.5 is usually set to a small value. For example 0.01 (Painton and Diwekar, 1995) or 0.001 (Chaudhuri and Diwekar, 1996). If this value is not small enough, the penalty function's rate of increase will be too fast. Hence, the penalty term will dominate the objective function (see Figure 7.11). A similar behavior can be observed for the case of the rate of increase constant k (see Figure 7.12). Resulting also in an increase in the number of iterations required (see Table 7.3)

As a result, a careful selection should be made of both weighting function parameters to avoid an excess in the number of configurations evaluated and a dominance of the penalty term. To accomplish this Painton and Diwekar (1995) suggest that the total penalty term should not go above approximately 10% of the objective function's magnitude. This can be verified by tracking the sizes of the penalty term and the objective function throughout the algorithm's implementation.

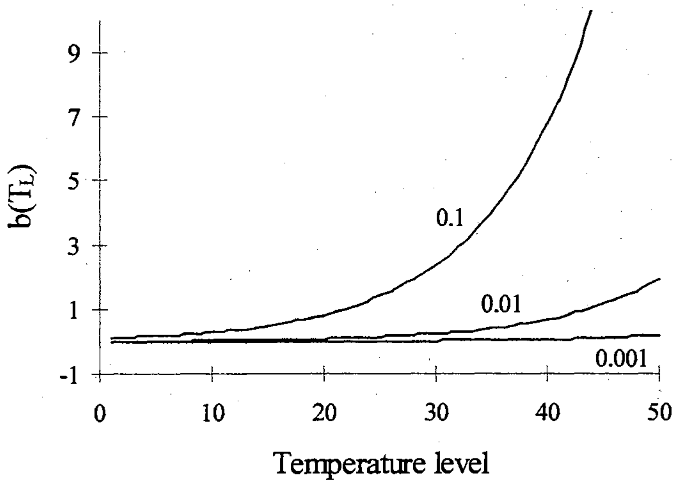

Figure 7.11: Effect of the weighting function constant

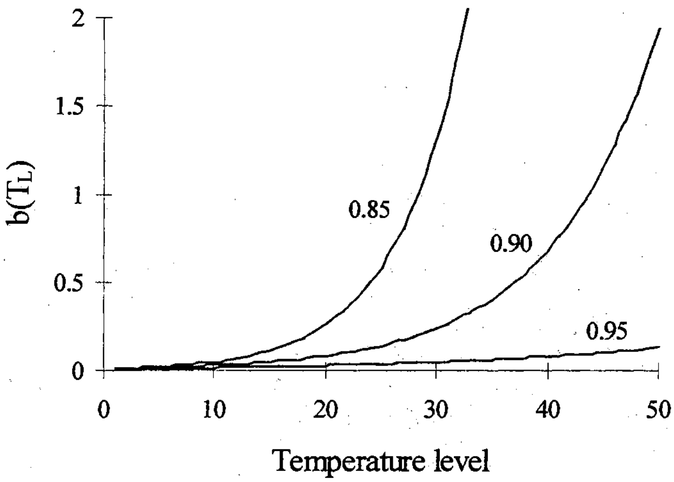

Figure 7.12: Effect of the rate of increase constant

Table 7.3: Comparison of different rate of increase constants[7]

Rate of increase constant *k*	Number of iterations
0.90	16,150
0.95	25,300
0.98	28,400

---

[7] The data presented in Table 5.4, corresponds to the solution of the methyl chloride example using an initial temperature of 25.

7.3.3 SPECIFICATION OF NEIGHBORHOOD MOVES AND SAMPLING PROCEDURES

The neighborhood moves should correspond to a Markov chain which is described as a series of random events, where the occurrence of each event depends only on the preceding outcome. For the case of the discrete or binary variables rule Chaudhuri and Diwekar (1996) describe the neighborhood moves using the following rule:

$$y_i^1 = \begin{cases} 1 & \text{if } y_i^0 = 0 \\ 0 & \text{if } y_i^0 = 1 \end{cases} \tag{7.6}$$

However, the use of this rule failed in evaluating a large portion of the feasible region, that can result in the identification of a local optimum instead of a global one[8]. To avoid this caveat and to get a better screening of the feasible region, the decision rule in Equation 7.6 was replaced with Equation 7.7.

$$y_i^1 = \begin{cases} 1 & \text{if } rand[0,1] > 0.5 \\ 0 & \text{if } rand[0,1] < 0.5 \end{cases} \tag{7.7}$$

For continuous variables, a move is defined as a random change for one variable. To accomplish this several move sequences are reviewed by Bohachevsky *et al.* (1986); Bohachevsky *et al.* (1995); Edgar and Himmelblau (1988); and Vanderbilt and Louie (1984). Chaudhuri and Diwekar (1996) propose that a random change should be made according to Equation 7.8.

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[8] To illustrate this consider an optimization problem with two continuous variables (x_1, x_2) and one discrete variable (y_1). Suppose that the current binary configuration is set to y_1=0, subsequent configurations to evaluate will only consider values for x_1 and x_2 for y_1=1. Unless a configuration is accepted at this condition all remaining configurations will be evaluated at y_1=1, failing to cover the complete search region.

$$x_i^1 = x_i^0 + (2 \times rand[0,1] - 1)S_{c,i} \tag{7.8}$$

where:

S_c = step size for continuous variable

The step size in Equation 7.8 represents a critical factor in the optimization problem and its magnitude depends on the properties of the objective function and on the desired accuracy and resolution (Bohachevsky *et al.*, 1985). A review of different methods available for estimating this parameter is given by Bohachevsky *et al.* (1995). For example, in an earlier work Bohachevsky *et al.* (1985) suggest that the step size should be such as to allow escape from a local minimum in a few (i.e., 2 or 3) steps. Based on this suggestion, the procedure used in this work to select the appropriate step size is given in Table 7.4.

Table 7.4: Procedure for selecting the step size

1. Select an initial step size using $S_c^0 = 0.1(U - L)$, where *U*= upper value of continuous variable and *L*= lower value of continuous variable
2. Perform the following loop at least 3 times
   (a) Calculate the new value for the optimization variable using Equation 7.8.
   (b) Determine the value of the objective function assuming no uncertainties are present in the model. That is evaluate *z* with the uncertain parameters fixed at a certain value (i.e. their average response).
3. Compare the values of *z* obtained (i.e. z_1, z_2, and z_3). If significant differences are observed then $S_c = S_c^0$. If not, select a new step size and return to Step 2.

The changes in the uncertain parameters as discussed in Section 7.2.3 is to be accomplished by sampling values from their distributions. These samples are generated by taking a random number from a uniform distribution and applying the respective transformation techniques (Banks and Carson, 1984; Law and Kelton, 1984; Park and Sharp-Bette, 1990).

The last move that needs to be specified relates to the number of samples to be taken as part of the stochastic annealing algorithm. That, as was described in Section 6.4.1, updates at each iteration this number using Equation 7.9.

$$\begin{array}{ll} \text{If } rand[0,1] \leq 0.5 \text{ then} & \\ & n_s = n_s + S_s \cdot rand[0,1] \\ \text{otherwise,} & \\ & n_s = n_s - S_s \cdot rand[0,1] \end{array} \tag{7.9}$$

The sample step size selected will impact the rate of increase in the number of samples generated for the stochastic annealing algorithm (see Figure 7.13). Even though this figure will change each time it is generated, the higher the step size the higher the rate of increase. To control this increase, Painton and Diwekar (1995) suggest using a value of 10, whereas in a parallel publication Chaudhuri and Diwekar (1996) employ a value of 7. This last number was employed in the present study.

Prior to finishing the present section an important note should be made regarding the initial values to use for each of the optimization variables —continuous or discrete— and for the sample size. For the former, their corresponding initial levels can be set either by their base case values or by generating a random initial configuration. For the

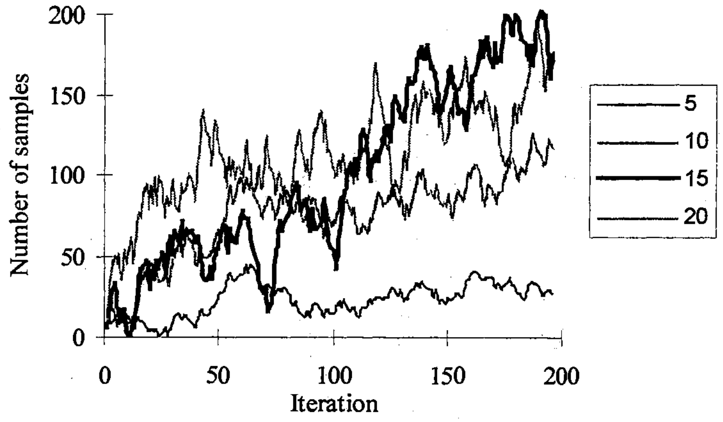

Figure 7.13: Effect of the step size for the number of samples

the sample size its initial value can be selected using a predetermined fixed number (i.e., 5) or through the aid of inference statistics (Pfaffenberger and Patterson, 1987).

7.4 MULTIOBJECTIVE STOCHASTIC OPTIMIZATION

The analysis of potential investment alternatives that seek to reduce the pollution generated within a chemical process will be done applying the stochastic annealing algorithm to find the best choice that maximizes the annual expected profit and minimizes the process' environmental impact. Within this context, this section presents the details of the stochastic annealing algorithm and how it can be applied using a process simulator such as ASPEN PLUS™. In doing so, it will be explained how the simple example used throughout the chapter was optimized.

The idea behind the implementation of the stochastic annealing algorithm using ASPEN PLUS™ can be seen in Figure 7.14. The initialization block sets the initial values for the control parameters. The optimization block is responsible for selecting the number of samples n_s and for generating the configurations to evaluate; that is it

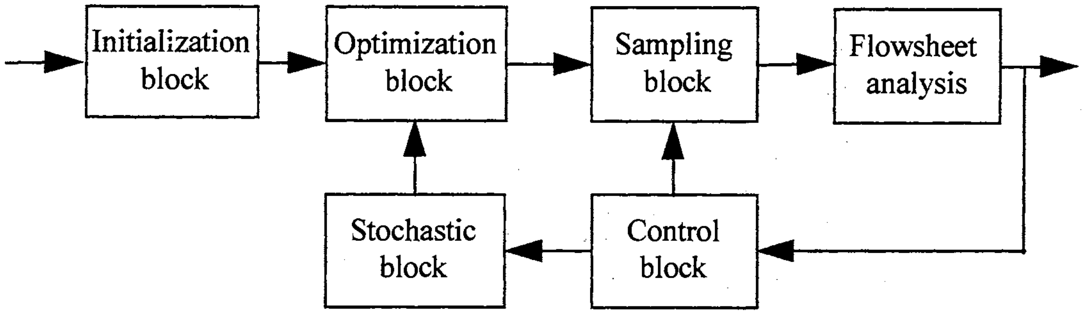

Figure 7.14: Stochastic annealing algorithm using ASPEN PLUS™

determines the new values for the optimization variables. The sampling block produces the values for the uncertain parameters and passes them to the flowsheet analysis blocks that runs the flowsheet model and determines the value of the objective function.

After the sampling and flowsheet analysis blocks have been repeated n_s times, the stochastic block generates the statistical information, the penalty function, and accepts or rejects the proposed configuration. Finally, a control block is used to control the overall performance of the algorithm.

Based on the simple diagram in Figure 7.14, on the previous section's discussion, and on the works by Chaudhuri and Diwekar (1996) and Painton and Diwekar (1995), the detailed algorithm for minimizing an objective function using the stochastic annealing algorithm and the process simulator ASPEN PLUS is presented in Figure 7.15.

To implement the algorithm in Figure 7.15, one needs to be able to evaluate the flowsheet model several times. This implies that the user has to have control over how many times the flowsheet is analyzed and the objective function calculated. In a typical programming language this is a straight forward task. However, with ASPEN PLUS this is not so easily accomplished. Hence, the approach suggested in this dissertation uses

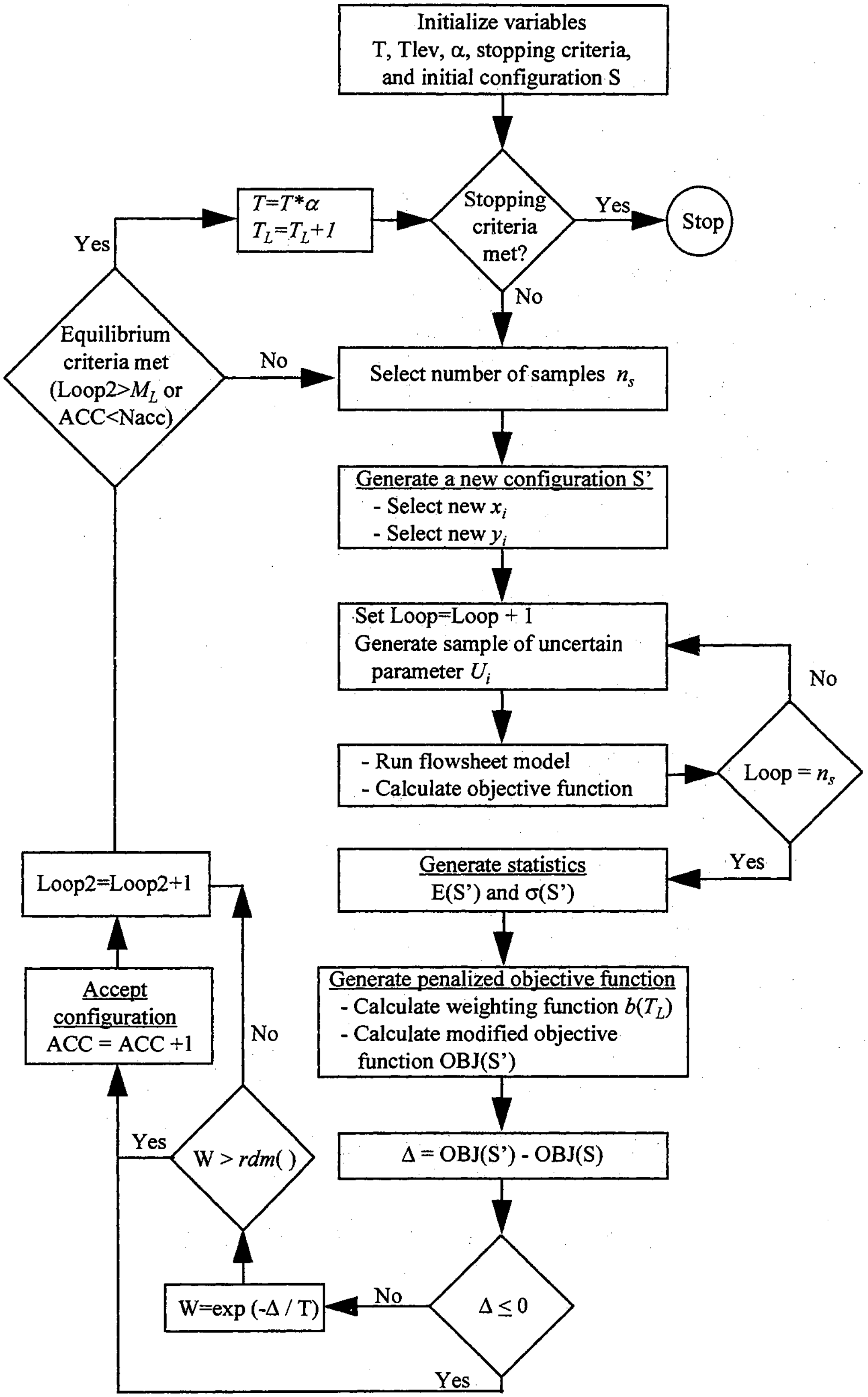

Figure 7.15: Stochastic annealing algorithm and ASPEN PLUS™: A detailed description

several dummy blocks and streams to force ASPEN to evaluate the model for a specified number of times. In this manner, three additional heater blocks (i.e. B1, B2, and B3) are added to the simple reactor system in Figure 7.4 (see Figure 7.16), and by constantly changing some of their parameters the simulator is tricked into performing a "DO LOOP" (see Table 7.5).

Consequently, the flowsheet is evaluated as many times as the temperature in block B3 is changed. It is important to mention that in order for the algorithm to work properly, the dummy blocks need to be situated at the beginning and end of the flowsheet, as shown in Figure 7.17, to force the complete model evaluation. To verify that this is being accomplished, the best approach is to generate a user specified convergence block like the following:

Table 7.5: Procedure for performing a DO LOOP using ASPEN PLUS

Step 1:	Use a counting variable to change the temperature in block B3.
Step 2:	Use a TRANSFER block (i.e. T-1) to copy the temperature of block B3 to the temperature of block B1.
Step 3:	Use block B2 to return the system's temperature to its input value.

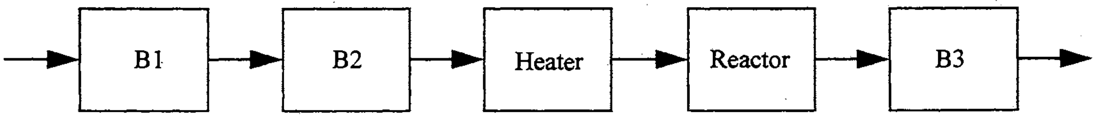

Figure 7.16: Modified reactor system for the manufacture of methyl chloride

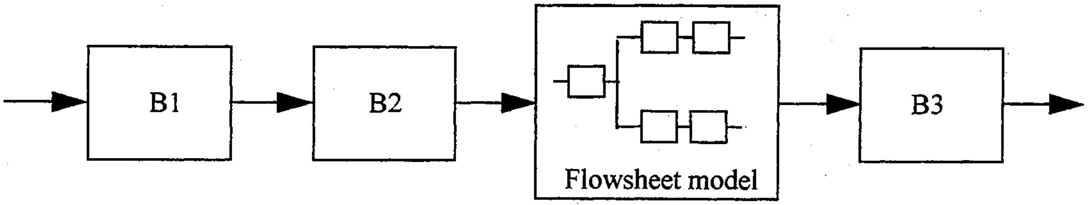

Figure 7.17: Generalized flowsheet model

```
SEQUENCE S-1 INIT C-1 B-2 CONTROL HX1 R1 STOC B3 T-1 B-1  &
        (RETURN C-1)
```

where:

S-1 = sequence id

C-1 = convergence block

INIT = FORTRAN initialization block

B1/B2/B3 = unit operation blocks (dummy)

CONTROL = FORTRAN control block

HX1 = unit operation block (heater)

R1 = unit operation block (reactor)

STOC = FORTRAN stochastic block

T-1 = transfer block

The block C-1 specifies the method used to converge the tear stream —unless otherwise suggested by ASPEN the one leaving Block B2— and to force the simulator to run a specified number of times. One should employ a method different from the default one since the limit of iterations will be set to a maximum. In this context, the method used was the direct substitution, setting its maximum allowable number of iterations to 9999. In most cases this limit will be exceeded, therefore the convergence block needs to be constantly initialized in a manual form. To better understand the stochastic annealing algorithm, the commented input file for the simple problem in Figure 7.16 is presented in Appendix D.

Throughout the algorithm's implementation it is required to produce random numbers for generating the new configuration, for sampling the uncertain parameters and for the implementation of the Metropolis algorithm. However, ASPEN PLUS™ does not have the capability of generating random numbers. Therefore, a random number generator function subroutine was included (see Appendix E)[9]. This subroutine is based on the algorithm proposed by Wichmann and Hill (1985) and requires three random seed numbers that can be found in a variety of statistical and mathematical texts.

Prior to finishing this section, a note should be made regarding the process constraints and the use of discrete or binary variables. Most of the process constraints, as previously mentioned, are specified internally by the simulator. However, if additional constraints are required as part of the optimization study design specification blocks and FORTRAN blocks can be used. In addition, a penalty function can be added to the objective function to represent specific constraints (Edgar and Himmelblau, 1988).

Finally, the handling of discrete variables was initially done using an FSPLIT block (Dantus, 1995). However, this considers the possibility zero flows to operating units within the flowsheet. This results in at least one flowsheet error[10] each time the simulator attempts to model the skipped unit. As a large number of iterations are

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[9] The random number function subroutine needs to be present in the same working directory where the flowsheet file is stored. In addition, the simulator's options should be changed to skip the in-line FORTRAN errors verification.

[10] Several errors can occur when the zero flow block is used in other flowsheet calculations, such as equipment costs estimates.

evaluated, these errors will eventually force the simulator to stop. Therefore, the discrete variables are to be handled using two manipulator blocks: duplicator and multiplier.

As can be seen in Figure 7.18, for each discrete variable a duplicator block is used before each possible option, followed by a multiplier block after evaluating the option. In this manner, the multiplier block is set to either "0" or "1" to represent the existence of the previous unit.

Finally, as shown in Figure 7.19 and previously in Figure 7.1 the analysis of source reduction alternatives using two criteria is undertaken under the compromise programming approach and the stochastic annealing algorithm. In this manner, the alternative selected will be the one that minimizes the expected distance from the ideal point (see Equation 7.10 and 7.11).

$$\min\ E(L_j) = \gamma^j_{AEP}\left(\frac{E(AEP^*) - E(AEP)}{E(AEP^*) - E(AEP^{**})}\right)^j + \gamma^j_\theta\left(\frac{E(\theta) - E(\theta^*)}{E(\theta^{**}) - E(\theta^*)}\right)^j \qquad (7.10)$$

$$\min(L_\infty) = \max\left[\gamma_{AEP}\left(\frac{E(AEP^*) - E(AEP)}{E(AEP^*) - E(AEP^{**})}\right), \gamma_\theta\left(\frac{E(\theta) - E(\theta^*)}{E(\theta^{**}) - E(\theta^*)}\right)\right] \qquad (7.11)$$

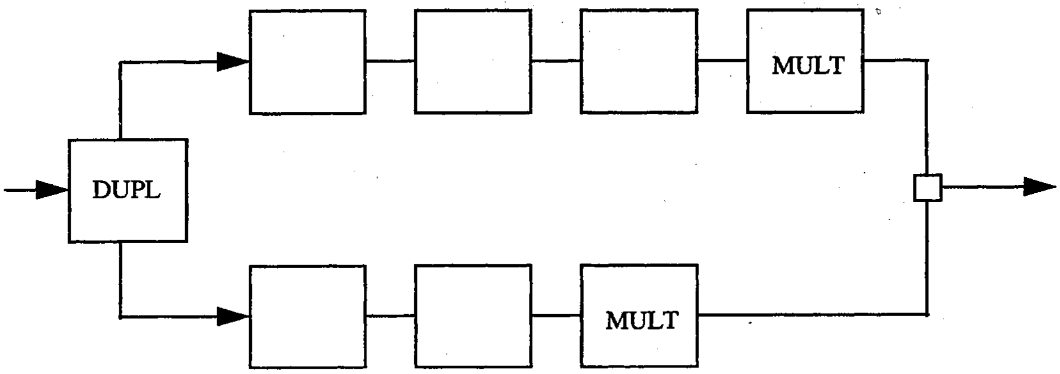

Figure 7.18: Binary variables using ASPEN PLUS™

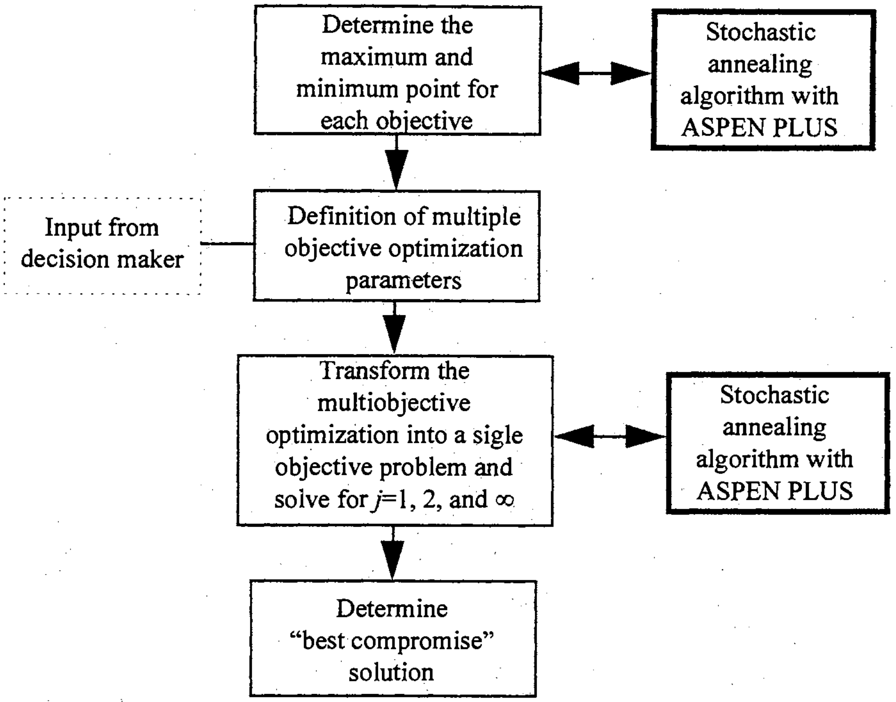

Figure 7.19: Evaluation of alternatives using a MOSO approach

To build the objective function in Equation 7.10 or 7.11 it is required to obtain the maximum and minimum points for each objective. That is the maximum and minimum expected value of AEP and the maximum and minimum expected value of θ. However, in most instances the minimum value of AEP could be set to 0. Alternatives having a negative AEP are not appealing to the decision maker. Once these points have been determined using the stochastic annealing algorithm, the objective function in Equation 7.12 and 7.13 is minimized for a value of $j = 1, 2$, and ∞, for the specific preference weights γ_i assigned to each objective.

7.5 SUMMARY

This chapter continued with the discussion of how the source reduction alternatives will be evaluated using multiple objective optimization techniques (MOSO), and presented the details of how this can be done using the process simulator ASPEN PLUS™. In summary, the main ideas to be taken out of this chapter include:

- Before evaluating the process alternatives using MOSO the analyst needs to define (1) the optimization variables and uncertain parameters and (2) the optimization parameters.
- The definition of optimization variables and uncertain parameters is accomplished through a three step procedure:
    1. Identification phase: Consist in listing the discrete and continuous variables, and the uncertain parameters. The identification is done using the techniques in Section 3.5 and/or a cause-effect diagram.
    2. Screening phase: The screening of optimization variables and uncertain parameters is done using experimental design techniques.
    3. Definition of ranges: Defines the ranges for the optimization variables and the distribution type used to represent the uncertain parameters.
- The definition of optimization parameters includes three sets of parameters: cooling schedule, stochastic annealing parameters, and neighborhood moves.
- Cooling schedule:

    Temperature's initial value: An initial Markov chain is evaluated and if $\xi<0.8$ the temperature is doubled. This procedure is continued until $\xi>0.8$.

Stopping criteria: The criteria used is to stop the algorithm's execution when the change in 5 consecutive Markov chains is small.

Temperature function: Represents the rule for changing the current value of the control parameter. In this work, the temperature function used is given by Equation 7.4, where α_T=0.9.

Markov chain length: The algorithm continues evaluating configurations until 10 transitions have been accepted or until a maximum of 10*n* neighborhood moves have been made.

- Stochastic annealing parameters: These include the weighting function constant (usually set to a small value) and the rate of increase constant.
- Specification of neighborhood moves:

  Integer variables: Described by Equation 7.7

  Continues variables: Described by Equation 7.8

  Uncertain parameters: Samples are generated by taking a random number from a uniform distribution and applying transformation techniques.
- The MOSO algorithm used to evaluate pollution prevention alternatives using ASPEN PLUS™ was described in Figure 7.15 and 7.19. Its execution requires tricking the simulator into performing a "DO LOOP" (see Table 7.5) and using a random number generator subroutine (see Appendix E).

CHAPTER 8

CASE STUDY

8.1 INTRODUCTION

The previous chapters defined the methodology to be used in order to implement waste minimization programs. As presented in Chapter 3, this methodology consists of six steps: characterization of waste streams, evaluation of environmental impacts, development of process model, identification of pollution prevention alternatives, evaluation of pollution prevention alternatives, and implementation of such alternatives.

In this chapter, based on the original process given by AIChE (1966) and on previous work by Dantus (1995) and Dantus and High (1996), this six step procedure is used to analyze the process for the manufacture of methyl chloride through the thermal chlorination of methane[1]. The chapter presents the description of the process and the development of the base case model that is used as the starting point for the methodology to represent the process currently in operation.

8.2 PROCESS DESCRIPTION

Methyl chloride (CH_3Cl), also known as chloromethane and monochloromethane,

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[1] The methyl chloride process is used only as an example to see how the proposed methodology can be applied. Several processes should be evaluated to proof the applicability and reliability of the methodology

was produced for the first time by J. Dumas and E. Peligot in 1835 by the reaction of sodium chloride with methanol in the presence of sulfuric acid (Rossberg *et al.*, 1986). Nowadays, methyl chloride is primarily produced through two methods: the thermal chlorination of methane and the hydrochlorination of methanol. There have been several other methods that can be used for the manufacture of methyl chloride (DeForest, 1979; Holbrook, 1993; Rossberg *et al.*, 1986). The majority of these are of theoretical significance but are not applied commercially.

Most of the methyl chloride produced —almost 82%— is used for the manufacture of silicones, particularly as the starting point in the Rochow synthesis (Morreto *et al.*, 1985). Other uses include the manufacture of methyl cellulose ethers, quaternary ammonium compounds, herbicides, and butyl rubber. These uses, and particularly the silicone one, has produced a 2.5% per year growth in the methyl chloride market. In the future, growth estimates suggest that the demand for methyl chloride will continue to increase, and will reach 775 million pounds by the year 2001 (CMR, 1997).

8.2.1 PROCESS CHEMISTRY

The process for the thermal chlorination of methane involves the reaction of methane and chlorine to produce methyl chloride (see Equation 8.1).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{8.1}$$

Subsequent reactions give methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) (see Equations 8.2 to 8.4).

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl \tag{8.2}$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl \tag{8.3}$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl \tag{8.4}$$

The initial reactants —methane and chlorine— must be heated above 300 °C for the reaction to start (DeForest, 1979). Once the reaction is initiated, controlling the high heat of reaction becomes a decisive factor in successfully carrying out the process. In this context, the reactor is usually operated between 350 to 550 °C. However, the reactor should not be operated at temperatures above 550 °C since decomposition of the products may occur, leading to undesirable byproducts. In addition, the reaction with chlorine can get completely out of control leading to the evolution of hydrogen chloride (HCl) and the release of large amounts of carbon through pyrolysis. The latter is a very exothermic reaction, that quickly reaches explosive violence (Rossberg *et al.*, 1986). Therefore, to successfully control the reaction temperature, several techniques have been suggested, such as the use of low feed ratios of chlorine to methane, the inclusion of an inert diluent such as nitrogen, and feeding the reactants with a mixture of carbon tetrachloride and/or lighter chloromethanes (DeForest, 1979).

The methane feed to the reactor should not contain more than 100 ppm of impurities, excluding N_2 (DeForest, 1979). As Johnson *et al.* (1959) suggest, under certain conditions, such as high impurities and both low and high mole feed ratios, the process can yield vinyl chloride, vinylidene chloride, 1,2-dichloroethylene, ethylidene dichloride, methyl chloroform, ethylene dichloride, and trichloroethylene. Apart from the regulation status of these byproducts, they can generate subsequent problems during the separation sequence. Hence, an attempt should be made to avoid these impurities.

8.2.2 GENERAL PROCESS

The process for the thermal chlorination of methane process consists primarily of a reactor where the previous four reactions (Equations 8.1 to 8.4) take place. The reactor effluent is cooled to 25 °C and it is washed with water to remove the hydrogen chloride generated. This water becomes a waste stream that contains both HCl and small amounts of chloromethanes. This water can present subsequent problems, therefore its content in the process streams should be less than 50 ppm to minimize corrosion and to prevent hydrolysis and decomposition of the chloromethanes (DeForest, 1979)[2]. Subsequently, the water is removed from the chloromethanes mixture through a series of dehumidification towers containing sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4), thus generating several waste streams. Finally, the gas mixture is compressed and passed through a series of distillation columns to separate each of the products (see Figure 8.1).

8.3 BASE CASE MODEL

The process for the production of methyl chloride through the thermal chlorination of methane as reported by AIChE (1966) was taken as the current process in operation. The input variables given (see Table 8.1) were used to model the process using the sequential process simulator ASPEN PLUS™ (version 9.3-1).

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[2] For example, at 120 °C and 620 kPa methyl chloride saturated with water decomposes at the rate of 1 g/100 ml H_2O per hour (Holbrook 1993).

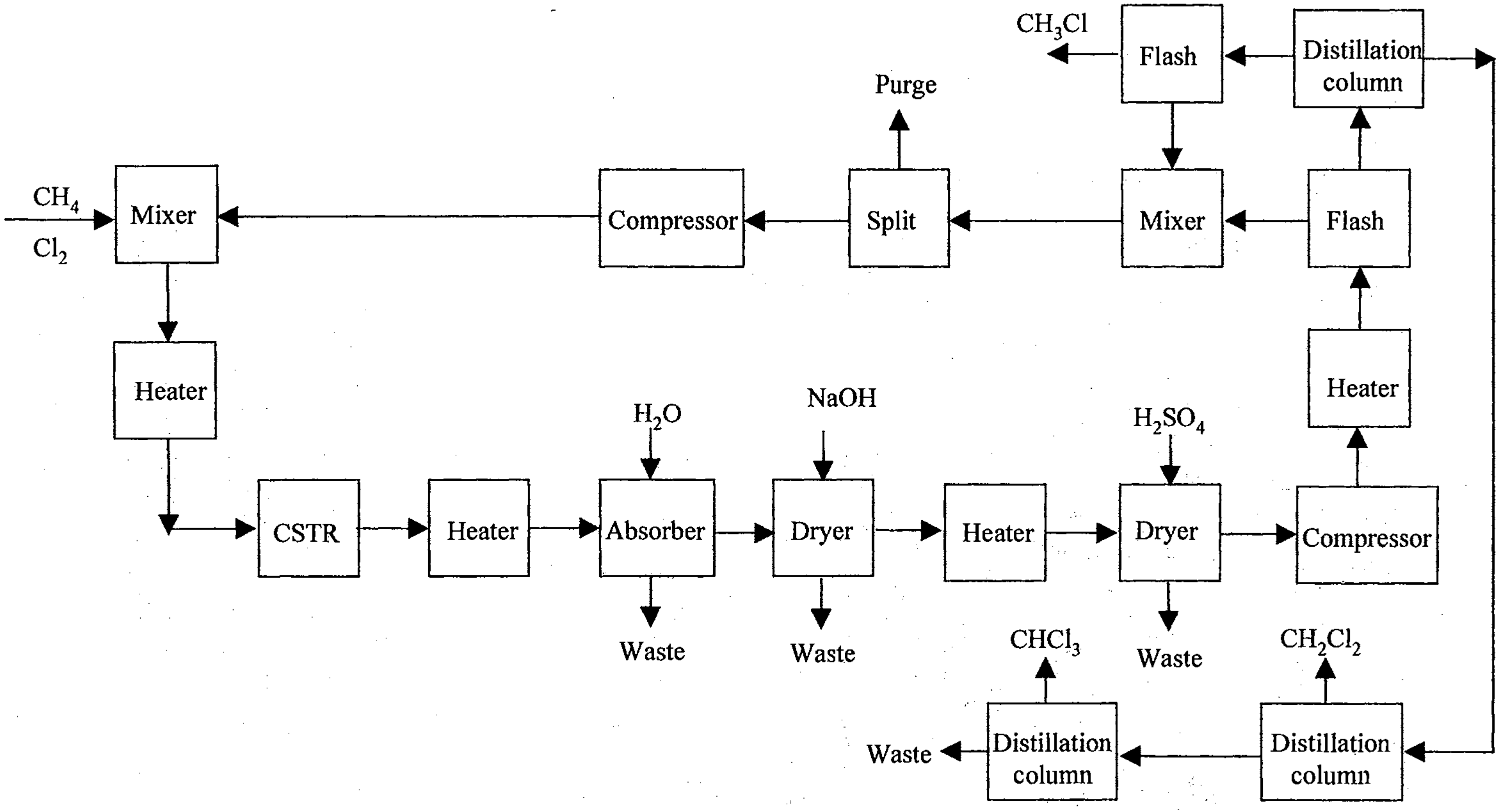

Figure 8.1: Methyl chloride base case process

Table 8.1: Reported input variables (AIChE, 1966)

Variable	Value
Feed ratio (Cl_2 / CH_4)	0.3
Reactor type	Isothermal CSTR
Reaction temperature	525 °C
Reactor effluent cooling system	25 °C
Condenser temperature	-50 °C
Compressor outlet pressure	7.8 atm

8.3.1 SYNTHESIS STEP

The synthesis step consists of a continuously stirred tank reactor (CSTR) where the four reactions take place (see Equations 8.1 to 8.4). This operation is modeled using the simulator's RCSTR block, that employs the power law expression to define the reaction kinetics (see Equation 8.5 and Table 8.2).

$$v = AT^{a} e^{-E_a/RT} \prod_{i=1}^{n} (Cn_i)^{b_i} \tag{8.5}$$

where:

v = rate of reaction

A = pre-exponential factor

T = temperature

a = temperature exponent

E_a = activation energy

Table 8.2: Kinetic parameters for base case model[3]

Reaction number	Rate Equation	Pre-exponential factor $\frac{m^3}{\text{kg mol-s}}$	Activation energy kJ/(kg mol)
1	$k_1[Cl_2][CH_4]$	2.56×10^8	82000
2	$k_2[Cl_2][CH_3Cl]$	6.28×10^7	71100
3	$k_3[Cl_2][CH_2Cl_2]$	2.56×10^8	82000
4	$k_4[Cl_2][CHCl_3]$	2.93×10^8	87200

R = universal gas law constant

Cn = concentration

b = concentration exponent

The product distribution will vary with temperature and feed ratio. As was shown in previous work (Dantus, 1995), the RCSTR block of ASPEN PLUS™ was used to determine the validity of the model by performing a product distribution study as a function of feed ratio and comparing it to other sources available (DeForest, 1979; Johnson *et al.*, 1959; McBee *et al.*, 1942; Scipioni and Rapisardi, 1961) (see Figure 8.2).

As mentioned previously, the methane feed —generally obtained from natural gas, coke oven gas, or gas from petroleum refining,— should not contain more than 100 ppm of impurities, excluding N_2. Any impurities present in the reactor might be chlorinated, generating undesired byproducts and inhibiting the production of the primary products. The reactions generating these undesired components should be incorporated as part of

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[3] Data taken from Dantus and High (1996) based on parameters reported by Scipioni and Rapisardi (1961).

the base case model in order to adequately consider the environmental impact of the process. However, the existence and number of these reactions can vary depending on the characteristics of the methane source and the mechanics of its purification. Therefore, since the methane separation is not to be included in this study, the methane feed will be assumed to contain 98% methane and 2% nitrogen[4]. Consequently, no additional higher carbon number chlorinated compounds will be considered.

8.3.2 SEPARATION STEP

The reactor effluent is cooled to the specified temperature of 25 °C and it is passed through an absorber to remove the hydrogen chloride generated, using water as the absorbing agent. For this reason, the dissociation of HCl in water, as well as that of the small amounts of chlorine present in the gas stream, need to be taken into account to accurately represent the absorber operation[5] (see Equations 8.6 to 8.9).

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^- \tag{8.6}$$

$$Cl_2 + 2H_2O \leftrightarrow H_3O^+ + Cl + HClO \tag{8.7}$$

$$HClO + H_2O \leftrightarrow H_3O^+ + ClO^- \tag{8.8}$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \tag{8.9}$$

---

[4] The nitrogen content in the methane feed was taken as the average of the N_2 concentration present in various natural gas sources (Corey *et al.*, 1984).

[5] As reported previously by Dantus (1995), the simulation of the absorber presented difficulties. Therefore, a relationship was used to determine the amount of water required as a function of the hydrogen chloride flowrate. Several enhancements were made to the RADFRAC module —the one used to simulate the absorber operation— in the latest ASPEN PLUS™ version; hence, in the present case, no empirical relationship between water and HCl was required.

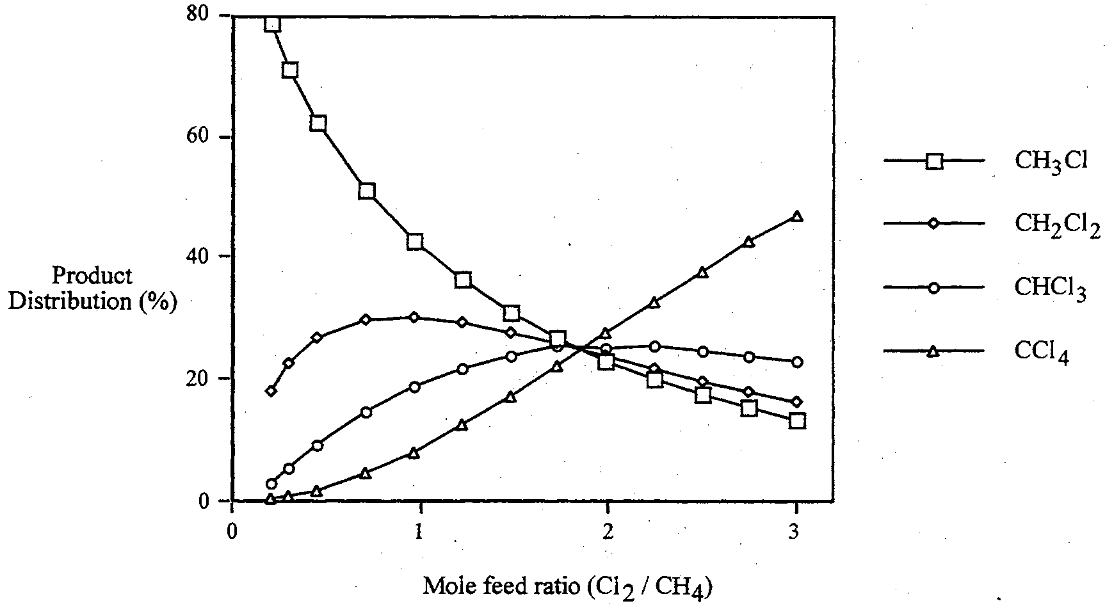

Figure 8.2 Product distribution as a function of feed ratio

The solution chemistry in Equations 8.6 to 8.9 uses the electrolyte Non-Random Two-Liquid (NRTL) and Henry's law models. The latter requires Henry's law constants for interactions between water and the different gas components. Even though, ASPEN PLUS™ has several data sources, it does not include parameters for the binary interaction between water and methylene chloride, chloroform, and carbon tetrachloride. In these cases, Henry's constants were calculated using Equations 8.10 to 8.12 (Gossett, 1987).

$$h_{\mathrm{CH_2Cl_2}} = \exp(6.653 - 3817/T) \tag{8.10}$$

$$h_{\mathrm{CHCl_3}} = \exp(9.843 - 4612/T) \tag{8.11}$$

$$h_{\mathrm{CCl_4}} = \exp(11.29 - 4411/T) \tag{8.12}$$

where:

h_x = Henry's constant for component x $\left(\mathrm{m}^3 \cdot \mathrm{atm/kg\ mole}\right)$

T = Temperature (K)

As was mentioned previously, the concentration of water throughout the process is recommended to be less than 50 ppm to minimize corrosion and to prevent hydrolysis and decomposition of chloromethanes. Therefore, the water introduced in the absorber needs to be removed before the gas stream enters the distillation sequence. This is generally accomplished using a series of drying towers that employ sodium hydroxide (NaOH) and sulfuric acid[6] (H_2SO_4). These towers were simulated in a similar manner as the absorber, using the solution chemistry given previously (see Equations 8.6 to 8.9) and the one presented in Equations 8.13 to 8.16.

$$\mathrm{NaOH} \leftrightarrow \mathrm{Na}^+ + \mathrm{OH}^- \tag{8.13}$$

$$\mathrm{NaCl} \leftrightarrow \mathrm{Na}^+ + \mathrm{Cl}^- \tag{8.14}$$

$$\mathrm{H_2O} + \mathrm{H_2SO_4} \leftrightarrow \mathrm{H_3O}^+ + \mathrm{HSO}_4^- \tag{8.15}$$

$$\mathrm{H_2O} + \mathrm{HSO}_4^- \leftrightarrow \mathrm{H_3O}^+ + \mathrm{SO}_4^{-2} \tag{8.16}$$

The final step in the separation step is a series of distillation columns where the product and the various byproducts are separated. These unit operations are modeled using the ASPEN PLUS™ rigorous simulation module RADFRAC, that employs the initial estimates obtained with the ASPEN PLUS™ DSTWU shortcut distillation method.

The synthesis step and the separation step are used to construct the base case model using the process simulator ASPEN PLUS™ (see Figure 8.1). A summary of the

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[6] In previous work (Dantus 1995), the drying towers were not simulated rigorously and their economic criteria was based on the amount of water to removed. However, to accurately represent the environmental performance of the process, their rigorous simulation was included as part of the base case model.

blocks used to represent the operating units is shown in Table 8.3, and the input file corresponding to the base case is given in Appendix F.

8.3.3 CHARACTERIZATION OF WASTE STREAMS

The purpose of this phase is to identify the streams that can represent an important potential environmental impact, a possible target for environmental regulations, and/or an important cost effect. In this context, the results obtained from the base case model are used to characterize process streams by source, destination, flowrate, composition, and properties (see Appendix G, Table G.1). The streams included in Table G.1 correspond to the feed streams to the process, as well as the product, waste, and recycle streams. In addition, four intermediate streams —those entering and leaving the reactor, the stream leaving the HCl/H_2O recovery system, and the stream entering the distillation sequence—were included in the characterization phase.

Table 8.3: Summary of base case blocks

Operating Unit	Block used
Reactor	RCSTR
Cooling/Heating system	HEATER
Absorber	RADFRAC
Dryer	RADFRAC
Condenser	HEATER
Compressor	COMPR
Distillation Columns	RADFRAC

8.3.4 EVALUATION OF ENVIRONMENTAL IMPACTS

The chemicals identified in the characterization study are used to identify the potential environmental impact of the different streams. To accomplish this, the chemical components were checked against the list of regulated chemicals that are considered to be potentially hazardous to the environment or to the human health (see Table G.2).

To aid in the identification of possible source reduction initiatives, a specific chemical flowsheet (SCF) was developed for each of the chemicals in Table G.2 (see Figures G.1 to G.9). Under the SCF approach, a stream is considered to be part of a path if the concentration of the chemical is greater than a reference concentration. Since, the chlorinated products are all considered hazardous wastes under RCRA, any amount present in a particular stream will render it as a hazardous mixture. Hence, their reference concentration was set to the smallest amount detectable. For the case of hydrogen chloride, a process specification is to eliminate its presence in the process, therefore a small reference value was also employed. A similar value was set for the remaining chemicals, due primarily to their hazardous characteristics.

8.3.5 ANALYSIS OF BASE CASE PERFORMANCE

Before continuing with the identification of pollution prevention alternatives, the base case model is evaluated with respect to its economic performance and its environmental impact. That is, with the two criteria employed to analyze waste minimization projects.

The economic performance for the base case, as was described on Chapter 5, is measured based on a five tier approach: usual costs, direct costs, hidden costs, liability costs, and less tangible costs. The usual costs encompass two types of expenses: the total fixed capital investment and the production costs. For the base case, it is assumed that all required equipment is currently in operation and it has been fully depreciated . Hence, no fixed capital investment is considered for the base case. On the other hand, the manufacturing cost items described were estimated using the economic data in Table G.3.

The direct costs include the capital, operating, material, and maintenance costs involved in the treatment, recycling, handling, transportation and disposal of waste. As was shown in Table G.1 and Figure 8.1, the base case process contains four waste streams: the stream W2 leaving the absorber, the streams W3 and W4 leaving the first and second drying columns respectively, and the purge stream WPRG affecting the recycle loop. However, the characterization of waste streams can be affected by several factors. For example, the stream W5 containing primarily carbon tetrachloride could initially be classified as a product stream. This categorization is set to change since a ban on CCl_4 production went into effect in 1996. Hence, the W5 stream will eventually become a waste stream.

Furthermore, some waste streams, such as the hydrogen chloride and water mixture, might undergo a certain amount of treatment to be considered as a by-product and a potential source of income. For a 95% recovery the expenses associated with the HCl/H_2O mixture were taken from Zimmer and Guaitella (1976). This information was updated and scaled using the Holland correlation (Holland *et al.*, 1974).

The remaining waste treatment and disposal costs for a given treatment efficiency were taken from Dyer and Mulholland (1994) and Cressman and Martin (1993). The hidden costs were assumed to be 100,000 $/year based on the information in Appendix A and on the discussion in Section 5.4. The fines and penalties were calculated using Equation 5.8 and the median expected values given in Table 5.5. And due to a lack of specific information, the future liabilities and the less tangible benefits were not included in the analysis.

Based on the economic model a preliminary analysis of the base case scenario estimates an annual equivalent profit of approximately 2,200,000 \$/yr. However, if all the waste related costs are taken into account, the process is really experiencing a loss translated into an annual equivalent profit of -130,000 \$/yr.

The second measure used to evaluate the base case model performance is its environmental impact calculated using Equation 4.6, where the release factor for the waste streams was set to 1, whereas an initial value of 0.1 was assigned to the non-waste streams. With respect to the chemical indexes used to calculate the process' overall environmental impact, they were calculated as described in Section 4.5.2 using the toxicity data given by Davis *et al.* (1994) and Bouwes and Hassur (1997b) (see Table 8.4). These values —assuming the missing endpoints are set to 0— produce an environmental impact of approximately 1100 EIU/ kg of CH_3Cl, for the base case process.

Finally, as one looks at the different assumptions and factors considered during the development of the economic and environmental impact model, the possibility of including them as uncertainties becomes increasingly important, so as to correctly evaluate the performance of the base case process and subsequently compare it to the source reduction alternatives.

Table 8.4: Chemical impact indexes for base case process[7]

Chemical	Environmental impact index (EIU/kg)		
		Missing endpoint data set to 0	Missing endpoint data set to 5
Carbon tetrachloride	72.2		
Chloroform		67.8	59.8
Methylene chloride		51.8	40.5
Methyl chloride		34.7	16.1
Chlorine		89.5	77.5
Sulfuric acid		100.4	70.4
Hydrochloric acid		80.2	74.0
Sodium hydroxide			
Methane			
Water	0		

8.4 IDENTIFICATION OF POLLUTION PREVENTION ALTERNATIVES

The selection of pollution prevention alternatives, as discussed in Chapter 7, is accomplished through a three step procedure: (1) the identification phase, (2) the screening phase, and (3) the definition of ranges phase. All of these phases, and in particular the first one, require a creative process and can be repeated several times until all feasible alternatives have been identified.

Based upon the analysis of the base case model combined with the phases of characterization of process streams and evaluation of environmental impacts, the present section discusses the identification of an initial set of waste minimization options. This

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[7] No toxicological data was available for sodium hydroxide and methane. Hence, it was not possible to estimate their environmental impact indexes. The lack of this information was considered as a source of uncertainty.

set considers only technology changes[8] and it is not intended to represent all the possible source reduction projects, its main purpose is to serve as an example of how they are to be selected, screened, and finally optimized.

8.4.1 IDENTIFICATION AND SCREENING PHASES

The analysis of the base case model combined with the phases of characterization of process streams and evaluation of environmental impacts, are used to identify possible source reduction alternatives. There are numerous ways to generate these alternatives: structured thinking methods (Douglas, 1985; El-Halwagi and Manousiouthakis, 1989; Linnhoff, 1994), lists of potential ideas (Chadha, 1994; CMA, 1993; Doerr, 1993; Dyer and Mulholland, 1998; Nelson, 1990; Siegell, 1996), and cause-effect diagrams (see Sections 3.5 and 7.2.1).

In the present study, a structured thinking method approach was primarily followed combined with the information generated during the identification of environmental impacts' phase and with the aid of the specific chemical flowsheets in Appendix G. During this analysis, it can be observed that one of the main factors affecting the process economic performance and environmental impact is the production of the by-products inside the reactor. Therefore, two initial alternatives are identified: (1) change the operational settings of the reactor, and (2) change the type of reactor (i.e. a plug flow reactor).

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[8] Within the realm of waste minimization techniques technology changes include process changes; equipment, piping, or layout changes; and changes in operational settings (see Figure 2.5).

The second important factor represents the initial split of the reactor effluent that determines the separation system's performance. In this case, both the temperature and pressure of this operation are considered as potential changes in operational settings.

The list of possible uncertainties to consider in the evaluation of the previous alternatives can be quite extensive in particular since no experimental data or physical plant information was available. Therefore, as an example of the methodology's application —keeping in mind the uncertainty sources in the analysis of waste minimization projects (see Table 4.1)— uncertainties were considered in the process model (i.e., kinetic constants), in the environmental impact model (i.e., release factor and specific chemical impact index), as well as uncertainties due to external factors (i.e. utilities costs).

In summary, the initial set of waste minimization options consists of five continuous variables, one discrete variable, and four uncertain parameters (see Table 8.5). Table 8.5 also includes the upper and lower values used in the screening of this initial set. This analysis was made using a fourth order 2_{IV}^{11-6} experimental design matrix to evaluate the effect of 11 variables on both objectives —*AEP* and θ—using 32 experiments[9].

The screening of the initial set of source reduction options using experimental design techniques identifies the following variables and parameters to consider further in the evaluation of pollution prevention alternatives' phase: the temperature of the original reactor (TCSTR), the mole flow of chlorine (FCl_2), and the use of an alternative reactor (YPFR) and its operating temperature (TFPR). In addition, as can be seen in Table 8.6,

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[9] The experimental design analysis was performed as described previously in Table 7.1. In addition, a brief example of how this analysis is applied is given in Appendix C.

Table 8.5: Definition of optimization variables and uncertain parameters used in the experimental design analysis

Variable description	Variable type	Base case value	Upper level (+)	Lower level (—)
Temperature of CSTR (TCSTR)	Continuous	525 °C	550° C	470 °C
Separation system compressor pressure (Block CMP1) (PCMP1)	Continuous	7.8 atm	8.6 atm	7 atm
Separation system initial temperature (Block HX4) (THX4)	Continuous	-50 °C	-45 °C	-55 °C
Temperature CH_4/CH3Cl separation (Block FL2) (TFL2)	Continuous	-73 °C	-67 °C	-79 °C
Mole flow of Cl_2 (FCl_2)	Continuous	145 kgmol/h	160 kgmol/h	130 kgmol/h
Alternative reactor's operating temperature (TPFR)	Continuous	525 °C	550° C	470 °C
Type of reactor (YPFR)	Discrete	1	1	0
Release factor for non-waste streams (RFS)	Uncertain	0.1	0.3	0.1
High pressure steam price (HPSP)	Uncertain	0.01 \$/kg	0.012 \$/kg	0.008 \$/kg
Pre-exponential factor for reaction 6.1 $\left(m^3/\text{kg mol - s}\right)$ (PREXP)	Uncertain	2.56×10^8	2.81×10^8	2.3×10^8
Environmental impact index for CH_3Cl (EICH)	Uncertain	34.7	34.7	16.1

Table 8.6: Screening results of optimization variables and uncertain Parameters using experimental design techniques[10]

Variable	Effect on θ	Effect on *AEP*	Optimization Range	Distribution type
TCSTR	-24	**142,220**	350 - 550 °C	
PCMP1	-9	-11,780		
THX4	12	27,320		
TFL2	1	-13,250		
FCl_2	**131**	**2,179,300**	130 -160 kgmol/h	
TPFR	-11	**-189,900**	350 - 550 °C	
YPFR	**121**	**-882,227**	0 - 1	
RFS	**299**	17,489		Triangular distribution with: M_o=0.1, *Low* = 0.05, *High*=0.3
HPSC	-3	**-144,847**		Normal distribution with: μ=0.01 \$/kg σ= 0.002
PREXP	-37	**-119,236**		Normal distribution with: μ=2.56 x 10^8 σ= 8 x 10^6
EICH	**42**	-19,552		Uniform random distribution between 16.1 and 34.7

all uncertain factors were determined to be important during the optimization phase. This table also includes the optimization ranges to be used, as well as the different types of distribution assumed for the uncertain parameters.

8.5 EVALUATION OF POLLUTION PREVENTION ALTERNATIVES

The evaluation of the initial set of pollution prevention alternatives was done using the algorithm presented in Figure 7.1 and 7.19. As shown in Tables 8.5 and 8.6, these alternatives consisted of three continuous variables and one discrete variable influenced by four uncertain parameters.

The possibility of changing the type of reactor involves certain capital investment. This capital cost outlay was estimated using the ASPEN PLUS™ costing subroutine together with Equation 5.2 where α and β were set to 1.7 and 0.15 respectively.

Consequently, the final flowsheet evaluated is obtained by incorporating the various process alternatives into the base case model (see Figure 8.3). The flowsheet in Figure 8.3 is further modified to include the blocks necessary for the implementation of the stochastic annealing algorithm (see Figure 8.4 and Appendix H). The final input file in Appendix H contains the base case process, the respective source reduction alternatives, the three additional dummy blocks, and the initialization, control, stochastic, and transfer blocks.

The parameters required for the algorithm's implementation, including those related with the cooling schedule, the stochastic annealing algorithm, and the

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[10] The values in bold represent the factors having an important effect on the respective objective. For example, by changing the CSTR operating temperature one can expect an increase in the AEP of approximately 142,000 units.

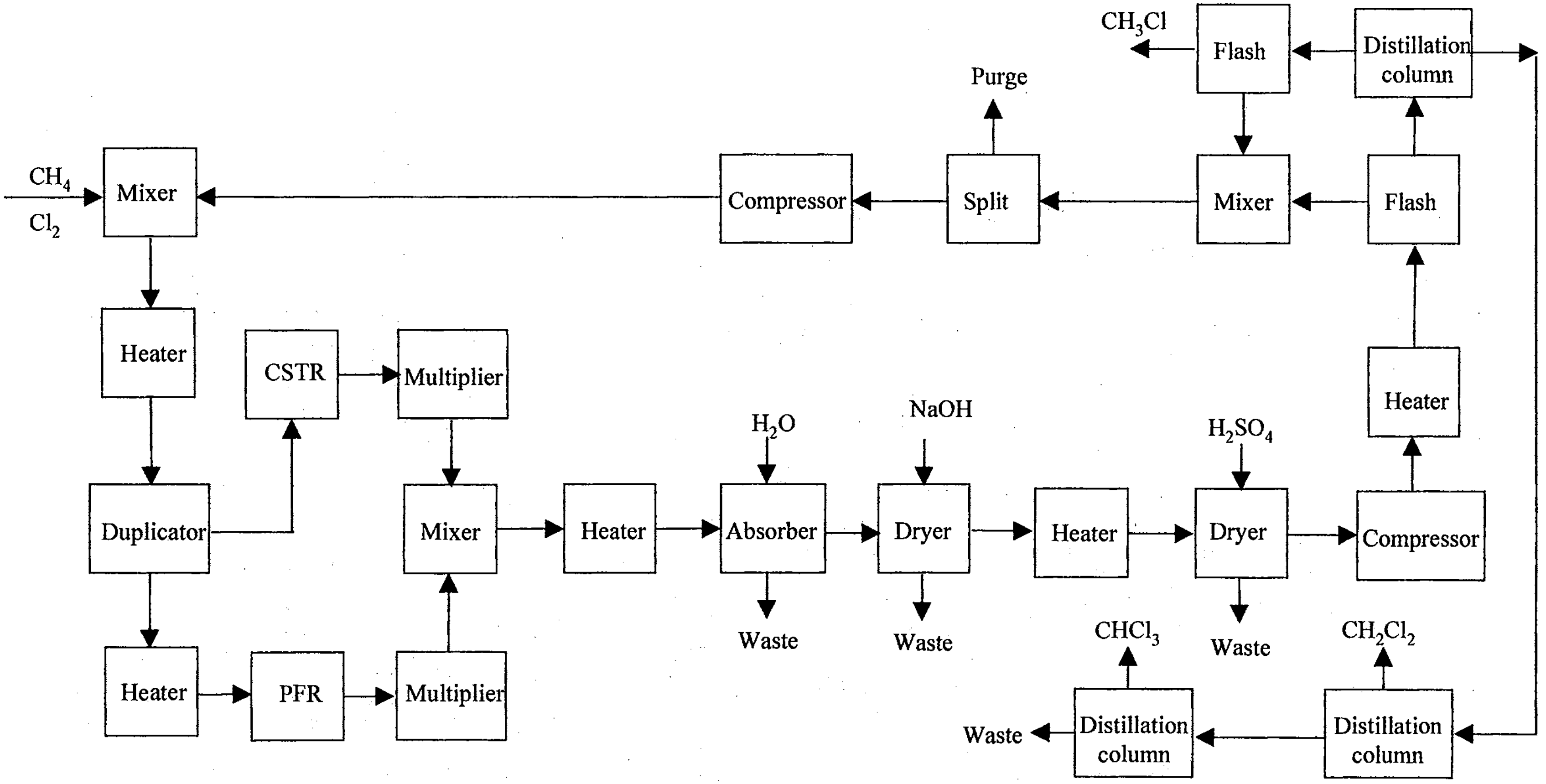

Figure 8.3: Methyl chloride optimization flowsheet

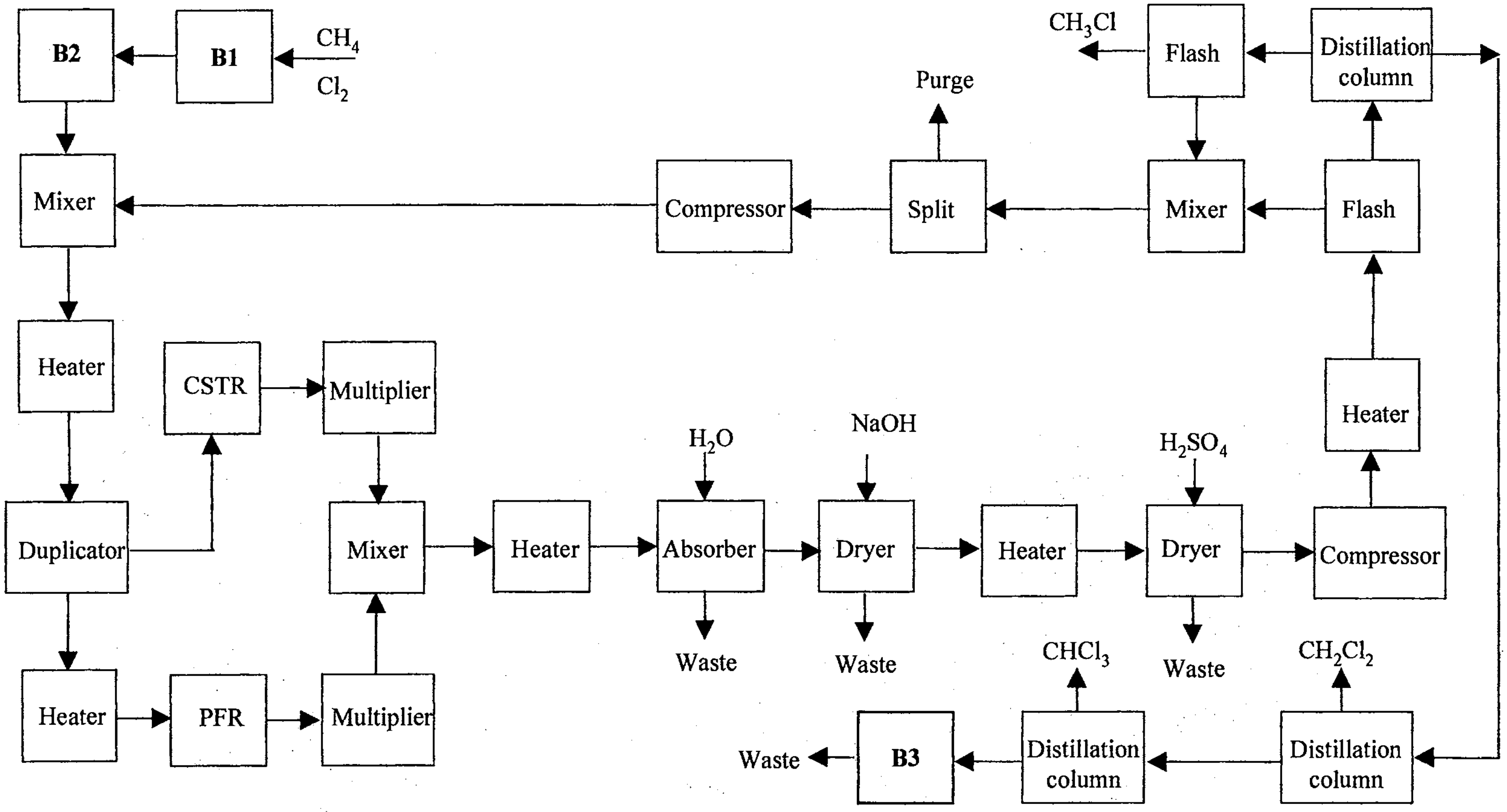

Figure 8.4: Methyl chloride modified optimization flowsheet

neighborhood moves were estimated and defined based on the procedure and discussions given in Chapter 7 (see Table 8.7). The initial values used for the optimization variables corresponded to a random permutation of the base case process' parameters and for the number of samples its initial value was set to 5.

As was shown in Figure 7.1 the first step towards implementing the multiple objective optimization approach is to estimate the best and worst performance of each decision rule using the stochastic annealing algorithm (see Table 8.8), where for the case of minimizing the AEP, its minimum value was set to 0 as discussed in Section 7.4.

During the calculation of the points given in Table 8.8 sporadic convergence problems occurred in the evaluation of the first drying column. This required the reinitialization of this block at each iteration[11] increasing substantially the computer time. Yet even with this approach, convergence problems —in a lesser amount— still persisted in particular since the block's performance is very sensitive to large variations in the feed conditions. As a result, after a large number of flowsheet evaluations in which this block was monitored, the original model used to represent this operating unit (rigorous fractionation model, RADFRAC) was replaced with a simple separation block assuming a 30% removal of the water present in the feed stream and maintaining the original sodium hydroxide requirements.

The information in Table 8.8 is used to build the final objective function (see Equations 8.17 and 8.18).

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[11] The term iteration does not imply only those related with the stochastic annealing algorithm. By reinitializing the drying column, this block returns also to its original value after each flowsheet pass used to converge the recycle structure.

Table 8.7: Case study's optimization parameters

Parameter	Value
Cooling schedule	
Initial "temperature"	For Max AEP T_0=200 For Min θ T_0=25 For Max θ T_0=25 For Min L_∞ T_0=10
Stopping criterion	Small change in 5 continuous Markov Chains
"Temperature" function	$T_{i+1} = 0.9T_i$
Markov chain length	Continue until number of accepted configurations = 10 or $M_L^{\max} = 10n$
Stochastic annealing parameters	
Weighting function constant (b_0)	0.01
Rate of increase constant (k)	0.9
Neighborhood moves	
Binary variables	$y_i^1 = \begin{cases} 1 & \text{if } rand[0,1] > 0.5 \\ 0 & \text{if } rand[0,1] < 0.5 \end{cases}$
Continuos variables	$x_i^1 = x_i^0 + (2 \times rand[0,1] - 1)S_{c,i}$ where: $S_{c,1} = 34$ $S_{c2} = 7$ $S_{c,3} = 34$
Number of samples step size (S_s)	$S_s = 5$

Table 8.8: Ideal point and worst case scenario[12]

Objective function	AEP \$ / yr	θ EIU / kg of CH_3Cl	x_1 °C	x_2 kgmol/hr	x_3 °C	y_1
Max AEP	869,300 ± 2,500	1089 ± 74.8	469.6	159.6	494.1	0
Min θ	-1,351,500 ± 2,700	986 ± 77.0	496.9	137.4	498.3	0
Max θ	-1,889,950 ± 2,500	1272 ± 70.4	477.5	138.8	481.1	1

$$\min\ E(L_j) = \gamma^j_{AEP}\left(\frac{E(AEP^*)-E(AEP)}{E(AEP^*)-E(AEP^{**})}\right)^j + \gamma^j_{\theta}\left(\frac{E(\theta)-E(\theta^*)}{E(\theta^{**})-E(\theta^*)}\right)^j \tag{8.17}$$

$$\min(L_\infty) = \max\left[\gamma_{AEP}\left(\frac{E(AEP^*)-E(AEP)}{E(AEP^*)-E(AEP^{**})}\right), \gamma_{\theta}\left(\frac{E(\theta)-E(\theta^*)}{E(\theta^{**})-E(\theta^*)}\right)\right] \tag{8.18}$$

These equation were solved for j=1, 2, and ∞, assuming equal weights to each objective, that is $\gamma_1=\gamma_2=1$; obtaining the results given in Table 8.9 and Figure 8.5. This last figure presents the location of the nondominated solutions with respect to the ideal point $\mathbf{z}^*$.

Analyzing the results given in Table 8.9, the decision variable y_1 should probably be set to 0, that is changing the reactor type generates a better performance on the process both from an environmental impact and economical perspective. The latter is improved even though additional capital investment is required.

Regarding the optimum values for the continuous variables, as for the case of the discrete ones, the final decision should be left to the decision maker that might select the

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[12] x_1=original reactor's operating temperature, x_2=chlorine mole flow, x_3=alternative reactor's operating temperature, and y_1=reactor type (1=original, 0=alternative).

Table 8.9: Optimization results for the methyl chloride process

j	Lj	AEP \$ / yr	θ EIU/ kg of CH_3Cl	x_1 °C	x_2 kgmol/hr	x_3 °C	y_1
1	0.353 ± 0.14	896,700 ± 36,900	1090 ± 62.2	388.5	159.7	487.7	0
2	0.444 ± 0.15	781,300 ± 1,900	1106 ± 56.8	435.6	159.4	506.7	0
∞	0.519 ± 0.075	774,150 ± 17,400	1097 ± 48.2	411.6	159.0	474.4	0

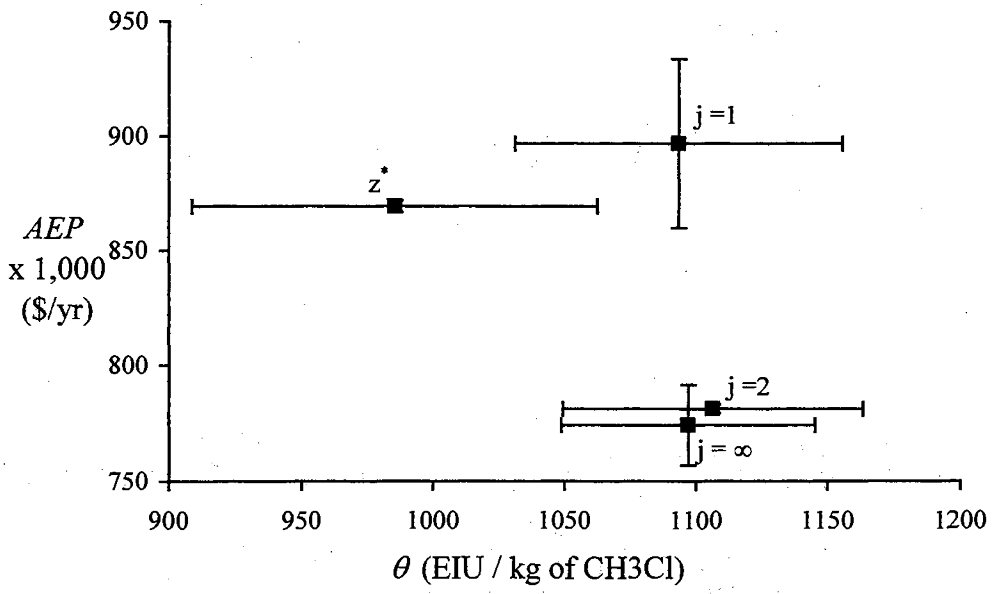

Figure 8.5: Multiobjective optimization results

best option based on his/her particular preferences. Given that equal weights to each objective were assigned, the best compromise solution is given when $j = 1$ in Table 8.9. That is, the best compromise solution is to operate an alternative reactor ($y_1 = 0$) at a temperature of 487.7 °C (x_3) using a chlorine flow of 159.7 kgmol/h, obtaining an expected annual equivalent profit of 896,700 ± 36,900 $/yr and an environmental impact of 1090 ± 62.3 EIU/kg of CH_3Cl.

A final note should be made about the $j = 1$ solution. Apparently, as shown in Figure 8.5, this compromise solution appears to be better than the ideal point $\mathbf{z}^*$ with respect to the annual equivalent profit. This situation can be in conflict with the definition of the ideal point. However, even though the $j = 1$ solution has a higher expected value of AEP it also has a higher degree of uncertainty in its value.

8.6 SUMMARY

This chapter presented an example of the application of the methodology proposed. The example consisted in the analysis of the process for the manufacture of methyl chloride through the thermal chlorination of methane. After describing the process analyzed, the chapter presented the development of the process model, the characterization of process streams, the evaluation of environmental impacts, and the identification and evaluation of process alternatives. In summary, the main ideas to be taken out of this chapter include:

- The deterministic performance of the base case process had an AEP of -130,000 $/yr (including all waste related costs) and an environmental impact of 1100 EIU/kg of CH_3Cl.

- The set of pollution prevention alternatives considered only technology changes and it was not intended to represent all the possible source reduction projects, its main purpose was to serve as an example of how they are to be selected, screened, and finally optimized.
- The initial set of waste minimization options consists of five continuous variables, one discrete variable, and five uncertain parameters.
- The screening of the initial set of source reduction options using experimental design techniques identified one discrete variable (reactor type), three continuous variables (original reactor's temperature, mole flow of chlorine, and the alternative reactor's operating temperature) and four uncertain parameters (release factor for non-waste streams, high pressure steam price, pre-exponential factor, and environmental impact index)
- The multiple objective stochastic optimization analysis identifies the use of an alternative reactor operated at a temperature of 487.7 °C using a chlorine flow of 159.7 kgmol/h, obtaining an expected annual equivalent profit of 896,700 ± 36,900 \$/yr and an environmental impact of 1090 ± 62.3 EIU/ kg of CH_3Cl.

CHAPTER 9

CONCLUSIONS AND FUTURE DIRECTIONS

9.1 CONCLUSIONS

The main objective of this work was to develop a comprehensive methodology that takes into account the uncertainties present when evaluating process alternatives that seek to reduce the waste generated in a chemical process. The procedure proposed consisted of six steps: characterization of waste streams, evaluation of environmental impacts, development of the process model, identification of pollution prevention alternatives, evaluation of pollution prevention alternatives, and their implementation (see Figure 9.1 and Table 9.1).

Even though the methodology was intended to be as general as possible, there were several aspects that remained to be defined for each particular application. For example, several factors within the identification of waste related costs, such as the less tangible benefits remained judgmental in nature. The generality question can also be raised since apparently the methodology was based on the application of a particular process simulator. However, enough details were given so as to apply it with several other process modeling tools. Furthermore, some of the methodology's building blocks were based primarily on US environmental regulations, yet the same concepts could be transformed into other environmental scenarios within the international community.

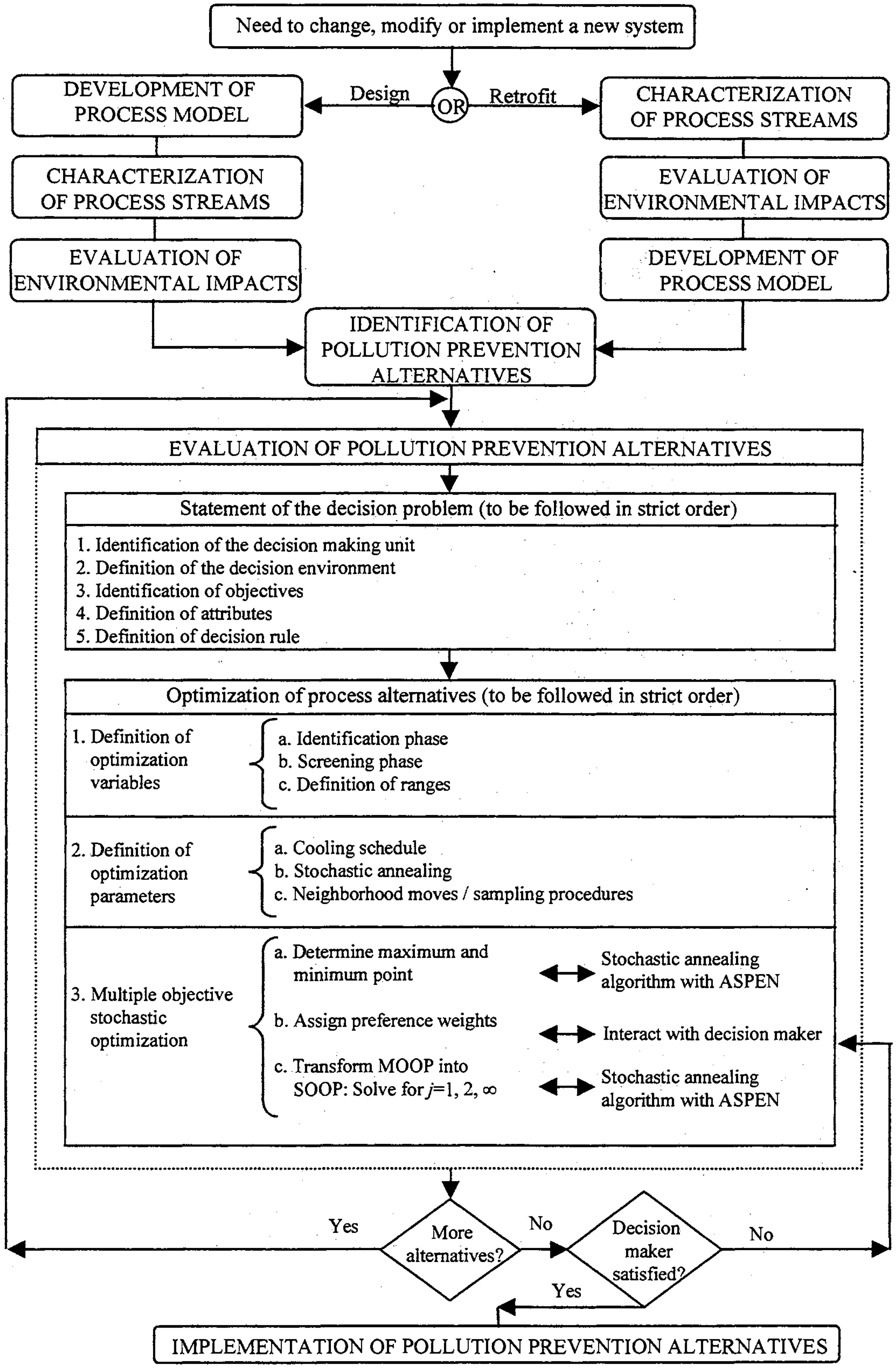

Figure 9.1: Outline of proposed methodology

Table 9.1: Summary of proposed methodology

1. CHARACTERIZATION OF PROCESS STREAMS: Process streams are characterized by source, destination, flowrate, composition, and properties.

2. EVALUATION OF ENVIRONMENTAL IMPACTS: Considers the identification of the potential environmental impact of the process streams incurred from the possible release to air, water, and land, as well as the chemical's regulatory status.

3. DEVELOPMENT OF THE PROCESS MODEL: The process model serves as an analysis tool to evaluate the performance of the current process, as well as an inexpensive experimental tool to examine the behavior of possible source reduction projects. The process model can be developed using a theoretical or empirical approach. In this work, the path taken is to develop a theoretical model with the aid of the process simulator ASPEN PLUS™.

4. IDENTIFICATION OF POLLUTION PREVENTION ALTERNATIVES: This step is usually accomplished with the use of hierarchical review approaches. One of the most important contributions is that of Douglas (1985). Two additional strategies mentioned are the heat and mass exchanger network analysis. Several other strategies for generating pollution prevention ideas were summarized in Table 3.3.

5. EVALUATION OF POLLUTION PREVENTION ALTERNATIVES: This step considers the evaluation of process alternatives to determine the best one to implement. The alternatives are evaluated considering their uncertainties using multiple objective stochastic optimization techniques to find the best feasible option among those evaluated.

    5.1. Statement of the decision problem

        5.1.1. Identification of the decision making unit (DMU): The DMU determines which if any of the alternatives is to be implemented. In this work, the decision to implement a pollution prevention project is assumed to be made by a single person.

        5.1.2. Definition of the decision environment: Decisions can be made under conditions of certainty, risk, uncertainty, or under a combination of the last two. In general, when dealing with uncertainty some amount of information is available or can be assumed. Therefore, in this work *the evaluation of source reduction alternatives will be made using methods suitable for making decisions under risk.*

        5.1.3. Identification of objectives: The objective of a decision problem is a statement that represents the desired state of the system that the decision maker is trying to obtain. Source reduction alternatives are to be evaluated using two competing objectives: *"maximize profit" and "minimize environmental impact."*

Table 9.1: Summary of proposed methodology (*Continued*)

5.1.4. Definition of attributes: The profit is measured using the *annual equivalent profit (AEP)* (see Section 4.5.1) taking into account the usual, direct, hidden, and liability costs and the less tangible benefits (the details of how these costs are calculated are given in Chapter 5). The environmental impact is measured using *a non-monetary valuation technique that incorporates toxicological data* and by including *a release factor* that is equivalent to calculating the probability of obtaining a release from a specific stream (see Section 4.5.2).

5.1.5. Definition of the decision rule: The *decision rule* that facilitates the ranking of the alternatives used is based on a *probabilistic approach*, selecting the alternative that maximizes or minimizes the expected value.

5.2. Optimization of process alternatives

5.2.1. Definition of optimization variables: The number of variables included in the optimization study, as well as the number of uncertain parameters can become a key factor in the complexity of the evaluation of source reduction alternatives. Therefore, a selection should be made as to which of these variables or parameters have an important effect in the process' performance. This is accomplished through a three step procedure.

5.2.1.1. Identification phase: Consist in listing the discrete and continuous variables, and the uncertain parameters. The identification is done using the techniques in Section 3.5 and/or a cause-effect diagram (see Figures 7.2 and 7.3).

5.2.1.2. Screening phase: The screening of optimization variables and uncertain parameters is done using experimental design techniques (see Table 7.1).

5.2.1.3. Definition of ranges: Defines the ranges for the optimization variables and the distribution type used to represent the uncertain parameters.

5.2.2. Definition of optimization parameters

5.2.2.1. Cooling schedule: Requires the specification of the initial value of the control parameter, the stopping criterion, a rule for changing the control parameter, and an equilibrium criteria.

5.2.2.2. Stochastic annealing parameters: Requires the specification of the weighting function constant and the rate of increase constant.

Table 9.1: Summary of proposed methodology (*Continued*)

5.2.2.3. Neighborhood moves and sampling procedures (see Section 7.3.3).

5.2.3. Multiple objective stochastic optimization: The evaluation of source reduction alternatives is made combining the compromise programming approach and the stochastic annealing algorithm (see Sections 6.3 and 6.4).

5.2.3.1. Determine maximum and minimum point using the stochastic annealing algorithm and ASPEN PLUS™ (see Figure 7.15).

5.2.3.2. Interact with decision maker and assign preference weights.

5.2.3.3. Transform MOOP into SOOP and solve for j=1, 2, and ∞ using the stochastic annealing algorithm and ASPEN PLUS™.

6. IMPLEMENTATION OF POLLUTION PREVENTION ALTERNATIVES: Once the feasible pollution prevention alternative has been evaluated and identified, the next step is to implement such alternative.

The methodology incorporated the use of multiple criteria decision making to evaluate possible investment projects using two competing objectives: maximize profit and minimize the environmental impact. The former is measured using the annual equivalent profit (AEP) tool and the latter using an environmental impact index. On one hand, the AEP included the usual costs associated with the process, as well as the various waste related costs, for which a detailed discussion was given including the different ways available to estimate them. On the other hand, the environmental impact index included toxicological characteristics of each chemical present in a process stream and its release potential.

Following the guidelines of decision theory, the decision to implement a source reduction project was considered as an individual decision making problem. However, the analyst or decision maker in general do not have all the necessary information to make the correct choice. This lack of knowledge or uncertainty should be incorporated in the decision making process. Yet, as shown in the methyl chloride process, the uncertainty increases the cost associated with the analysis of alternatives. So, is the increase in cost justified? The answer to this question depends on the type of process being evaluated and on the particular uncertainties considered. For example, in the methyl chloride process minimizing the environmental impact leads to the selection of an alternative reactor operated at 498 °C and a chlorine flowrate of 137.4 kgmol/h with an environmental impact of 986±77 EIU/kg of CH_3Cl. However, if no uncertainties are included in the optimization process the alternative reactor should be operated at 353 °C and a chlorine flowrate of 154.6 kgmol/hr with an environmental impact of 569 EIU/kg of CH_3Cl.

Multiple objective optimization techniques and stochastic programming methods were successfully incorporated in the methodology to evaluate the uncertainty in optimizing the two competing objectives. This was accomplished using the process simulator ASPEN PLUS™ (version 9.3-1) and combining the compromise programming approach and the stochastic annealing algorithm. However, the main obstacle encountered was the large computational requirements, in particular of the stochastic annealing algorithm. Even though a careful selection of its parameters was made, the method still required a large number of iterations to reach a solution. Each iteration involves the solution and evaluation of the complete process flowsheet, resulting in a computationally intensive analysis (e.g., each of the three points given in Table 8.8 took on average more than 140 hours to reach a solution).

The methodology was evaluated using the production of methyl chloride through the thermal chlorination of methane. Several other processes need to be evaluated to prove the applicability of the proposed methodology. The methyl chloride process was used mainly as a case study that was optimized considering three continuous variables, one discrete variable, and four uncertain parameters. The process was not intended to represent an actual process in operation. Therefore, the options analyzed represent only a small subset of a large number of possible source reduction alternatives.

Finally, one should also keep in mind that, as Schad (1998) states, a model does not guarantee a technically realizable process, and that a model is only as good as the input fed to it. Therefore, both the analyst and the decision maker need to be aware of the degree of accuracy of the model an the different assumptions used to develop it so as to reach the "correct" decision for the specific problem and for the particular decision maker.

In summary, the main accomplishment of this work is the development of a comprehensive methodology to identify and evaluate process alternatives that seek to reduce the pollution generated within the process. The methodology employs multiple objective stochastic optimization techniques to evaluate source reduction projects under uncertainty to select the best alternative that maximizes the project's profit and minimizes its environmental impact. This unique approach combines the compromise programming approach and the stochastic annealing algorithm to optimize waste minimization options using the process simulator ASPEN PLUS™.

9.2 FUTURE DIRECTIONS

As a more general methodology is developed for the chemical processing industry, there is still a great field of research to be conducted. Some of the research directions to consider in the future include:

- Apart from using an economical and environmental criteria to evaluate process alternatives, in the future the use of additional criteria might be considered. For instance it might be helpful to include factors such as safety, controllability, operability, and sustainability.
- Future research should also look at the possibility of using parallel computers to increase the speed of the optimization phase. At the same time, attention should be given to the screening phase in which the complexity of the model in terms of the number of variables and uncertain parameters can be reduced.
- Regarding the stochastic annealing algorithm's performance, future research could be directed first at looking at ways to enhance the stochastic annealing algorithm and consequently the simulated annealing approach. For example, a limit can be placed on the maximum number of random samples to be taken to estimate the expected value of the objective function. That is, there comes a point where given subsequent increases in this number, the objective function estimate is not improved sufficiently to justify additional flowsheet evaluations. Another possibility is to generate an approximate value of the objective function (e.g., n_s=5) and use a random procedure to determine if additional samples are required before initiating the Monte Carlo procedure.

This approach based on the algorithm suggested by Tovey (1988) can be used to reduce the number of flowsheet evaluations.

- Finally, in the future other processes should be evaluated so as to verify the applicability of the proposed procedure and consequently make any necessary adjustments. And if possible the procedure should be tested with a real case scenario.

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APPENDIX A

ECONOMIC EVALUATION TOOLS: A COMPARISON STUDY

A.1 TVM METHODS

Net present value

The net present value (NPV) criterion[1] evaluates the project's profitability by moving all its cash flows to a particular point in time: the present (see Equation A.1)

$$NPV = \sum_{n=0}^{Ny} \frac{F_n}{(1+i_r)^n} \tag{A.1}$$

where:

i_r = interest rate

F = cash flow

The cash flows in Equation A.1 consider both the positive cash flows due to revenues obtained, and the negative cash flows due to expenses or capital investments at the beginning of the project or throughout its operation.

The interest rate i_r in Equation A.1, also known as the discount rate, rate of return, minimum attractive rate of return (MARR), and annual discount rate represents the return on investment that a company expects on a particular project. The discount rate used varies from industry to industry. Some companies have a minimum fixed rate of return. Others consider the cost of capital, that is, what it would cost them to borrow money; while others decide their interest rate based on the return they could get from outside safe investments (Gable, 1992). In addition, different interest rates might be used

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[1] The net present value method is also knonwn as the net present worth, present worth, net present value analysis, net present value profit, venture worth, present worth amount, general present value model, discounted cash flow model, net discounted value, net discounted return, excess present value, and incremental present worth (Jelen, 1970; Morrow, 1991; Peters and Timmerhaus, 1991; Remer and Nieto, 1995a).

depending on the characteristics or riskiness of the investment[2]. For example, Ammann *et al.* (1995) comments on the use of a discount rate for environmental projects, that in general is lower than that of the company's general cost of capital. This is because as Ammann *et al.* (1995) suggest, the environmental projects usually have a lower risk. In any case, the discount rate used —that can be estimated using the capital asset pricing model (Brealey and Myers, 1988; Herbst, 1991)— considers the risk associated with an investment and will have an important effect in the NPV calculated[3] (see Figure A.1).

Once the discount rate is selected and the NPV calculated, the investment is evaluated based on the following acceptance criteria:

If NPV > 0	accept
If NPV = 0	remain indifferent
If NPV < 0	reject

The objective of any alternative project evaluation is to maximize the NPV, that is, to obtain the maximum return on a particular investment. Therefore, when comparing process alternatives the project that has the highest NPV is generally selected. It is important to point out, that when comparing alternatives equal time periods must be used. When dealing with unequal lives, the generally accepted procedure to apply is the replacement chain method (Ancel and Griffiths, 1996). This approach duplicates each

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[2] Although projects with the same degree of riskiness are easier to compare, in real situations this might not always be the case. In this context, Ancel and Griffiths (1996) present a simple procedure that can be used to compare projects with unequal risks where $i_{r,A}$ □ $i_{r,B}$. Their methodology based on the concept of crossover points is applicable also for unequal lives comparison.

[3] An intresting section dealing with the selection of the appropriate MARR is given in Park and Sharp-Bette's (1990) chapter 5.

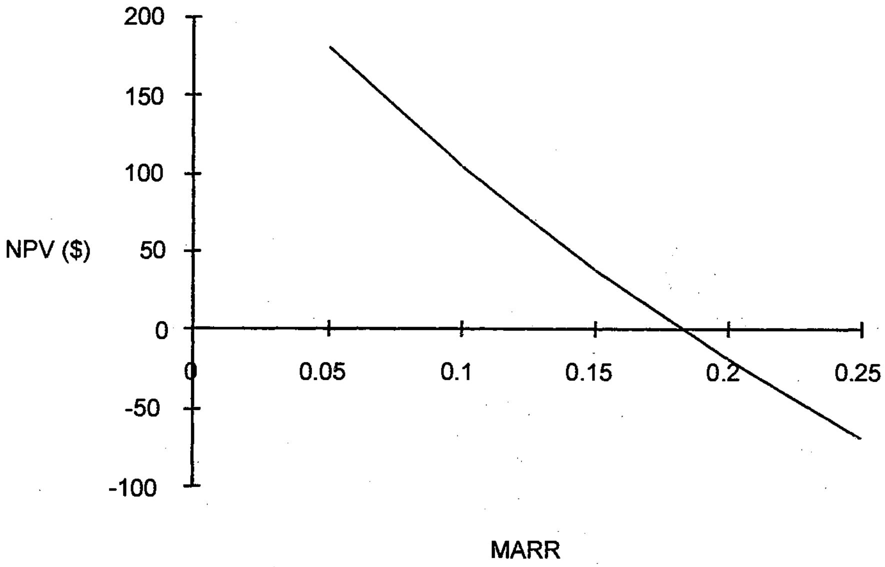

Figure A.1: Effect of i_r on the NPV calculated

project until a common life span is obtained. However, as Remer and Nieto (1995a) suggest, by replicating a project it is assumed that its cost remain constant throughout the comparison period. Depending upon the project, this assumption might be incorrect. In addition, as Ancel and Griffiths (1996) point out, when two projects are replicated a crossover point might exist, where there is a possibility of a reversal in the ranking of projects. Hence, the existence of such points should be considered.

There has been an increase in the popularity of the NPV method among industry. From 27 companies surveyed in 1978, only 52% reported using NPV; whereas in 1991, 97% of 33 companies reported using the NPV (Remer *et al.*, 1993). However, despite its popularity, one of the main disadvantages of this method lies in the fact the NPV gives no indication of the project magnitude (Weaver, 1991). That is, when comparing between alternatives, one project can have an investment several times that of the other; however, this difference might not be reflected when the NPV is calculated. In addition, some authors criticize the NPV method —in comparison with the internal rate of return (IRR)— by focusing in the difficulty to establish the correct discount rate, that will subsequently affect the project selection.

Future worth

The future worth (FW) method [4] can be considered a variation of the NPV tool; and it is therefore expected to have the same behavior, advantages, and disadvantages. In comparison to the NPV, the FW technique evaluates the project's profitability by moving all its cash flows to the future, generally at the end of the project's life (see Equation A.2).

$$FW = \sum_{n=0}^{Ny} F_n \left(1 + i_r\right)^{Ny-n} \tag{A.2}$$

combining Equation A.1 and Equation A.2, the FW is equivalent to

$$FW = NPV(1 + i)^{Ny} \tag{A.3}$$

Once the discount rate is selected and the FW is calculated, the investment is evaluated as was done with the NPV.

Annual equivalent profit

The annual equivalent profit (AEP)[5] is a variation of the two previously discussed methods, thus having the same acceptance criterion. Instead of moving all cash flows to

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[4] The future worth method is also known as the future worth cost, future cost, terminal worth, net future value, net future worth, and future value criterion (Park and Sharp-Bette, 1990; Remer and Nieto, 1995a).

[5] The annual equivalent profit evaluation tool is also known as the annual worth method, net equivalent uniform annual value criterion, annual equivalent criterion, equivalent uniform annual worth evaluation, annual worth analysis, equivalent uniform annual cost, equivalent uniform annual benefit, annualized cash flow method, levelized annual cash flow method, and net annual rate (Brealey and Myers, 1988; Remer and Nieto, 1995a; Stermole and Stermole, 1990).

the beginning or end of the project's life, this method converts them to a series of equal annual amounts using the annuity factor in Equation A.4 (Park and Sharp-Bette, 1990).

$$A_f = \frac{i_r(1+i_r)^{Ny}}{(1+i_r)^{Ny}-1} \tag{A.4}$$

where:

Af = Annuity factor

Combining Equation A.1 and A.4, the AEP is calculated using Equation A.5:

$$AEP = NPV(A_f) = \left[\sum_{n=0}^{Ny} \frac{F_n}{(1+i_r)^n}\right]\left[\frac{i_r(1+1)^{Ny}}{(1+i_r)^{Ny}-1}\right] \tag{A.5}$$

Although this method requires the calculation of the NPV, one apparent advantage is that the annual equivalent profit can be used regardless of the inequality of the projects' lives between the alternatives evaluated. However, as Ancel and Griffiths (1996) demonstrate for some instances the use of the AEP method incorrectly identifies the best option when dealing with different project lifetimes.

Net return rate

The net return rate (NRR) is an attempt to address some of the deficiencies of the NPV method, regarding differences in investment and lifetime. The NRR is calculated using Equation A.6 (Ward, 1994):

$$NRR = \frac{NPV}{I_D Ny} \times 100 = \frac{\sum_{n=0}^{Ny} F_n/(1+i_r)^n}{I_D Ny} \times 100 \tag{A.6}$$

The NRR does not change if the FW is used instead of the NPV, as long as the total depreciable capital I_D is correctly moved in time. A positive value of NRR represents a profitable project and can be used to compare process alternatives.

As Ward (1994) argues one of the main advantages of this method compared to the NPV is that it accurately takes the effect of the difference in project lives. However, when the NPV technique is correctly applied for unequal lives, the same result is obtained with both methods.

Profitability index

The profitability index (PI)[6] can be defined as the ratio of the present value of the future cash flows —without considering the initial investment— to the initial investment I_0 (Brealey and Myers, 1988) (see Equation A.7)

$$PI = \frac{\sum_{n=1}^{Ny} \frac{F_n}{(1+i_r)^n}}{I_0} \qquad \text{(A.10)}$$

where:

I_0 = Initial investment

Under this criterion, any project with a PI > 1, is judged acceptable, and is rejected with a PI < 1. The PI is expected to yield the same results as the NPV. However, its use can be misleading when comparing alternative investments (Brealey and Myers, 1988).

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[6] The profitability index is also known as the benefit-cost ratio, discounted return/investment ratio, ranking index, and savings to investment ratio (Brealey and Myers, 1988; Morrow, 1991; Remer and Nieto, 1995b; Winston, 1995).

Premium worth percentage

The premium worth percentage (PWP), also known as explicit reinvestment rate of return, discounted profit to investment ratio, and discounted return on original investment (Remer and Nieto, 1995b), is a variation of the profitability index. In this case, the PWP is defined as the ratio of the net present value —that includes the capital investment, as compared to the present value of the PI that does not include it— to the initial capital investment (see Equation A.8) (Remer and Nieto, 1995a)

$$PWP = \frac{\sum_{n=0}^{Ny} \frac{F_n}{(1+i_r)^n}}{I_0} \tag{A.8}$$

As with the previous techniques, the aim is to select the project that maximizes the value of PWP and that is judged acceptable based on the following criteria:

If PWP > MARR	accept
If PWP = MARR	remain indifferent
If PWP < MARR	reject

Internal rate of return

The internal rate of return (IRR)[7] has been one of the most used methods in evaluating project profitability. However, a decrease in its use compared to the NPV tool has been reported (Remer *et al.*, 1993). In theory, both the IRR and NPV will give the

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[7] The internal rate of return is also known as the rate of return on discounted cash flow, profitability index, interest rate of return, true rate of return, investors rate of return, discounted cash flow rate of return, return on investment, investor's method, break-even rate of return, rate of return, discounted cash flow return on investment, discounted cash flow, and the yield method (Jelen, 1970; Lefley, 1997; Peters and Timmerhaus, 1991; Remer and Nieto, 1995a; Stermole and Stermole, 1990; Woinsky, 1996).

same answer when comparing investment alternatives. This is true whenever the NPV of a project is a smoothly declining function of the discount rate (Brealey and Myers, 1988) (see Figure A.1).

The IRR can be defined as the discount rate that equates the net present value of all cash flows to zero. This criterion is evaluated by setting Equation A.4 to zero and solving iteratively for *IRR* (see Equation A.9)

$$NPV = \sum_{n=0}^{Ny} \frac{F_n}{(1+IRR)^n} = 0 \tag{A.9}$$

Once the interest rate *IRR* is calculated, it is compared to the established minimum attractive rate of return (MARR) and the project's profitability is evaluated in the same way as with the PWP method. One of the problems of the IRR technique is the possible existence of multiple roots in Equation A.9 (see Figure A.2). In order to determine the feasibility of multiple roots, Descartes' rule or the Norstrom criterion can be employed (Park and Sharp-Bette, 1990). These criteria measure the number of real positive roots based on the number of sign changes in the coefficients of the polynomial or in the cash flow series. When multiple roots exist, the IRR method should not be employed. In this case, Morrow (1991) suggests the use of a modified internal rate of return that moves the future negative cash flows to the beginning of the project; therefore, having only one sign change in the cash flow series. However, this approach requires specifying an interest rate to be able to move the negative cash flows.

Regarding investment comparisons, the IRR method should only be used when comparing two projects (Weaver, 1991). For an array of possible alternatives, this

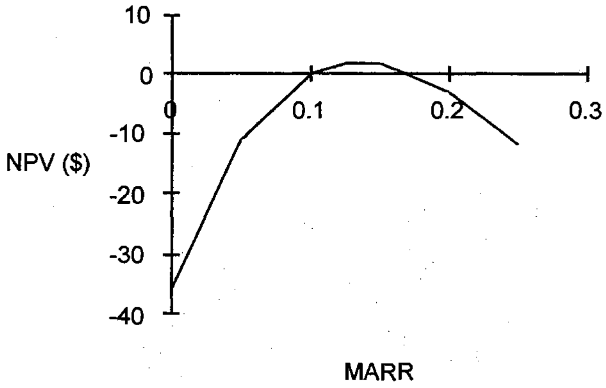

Figure A.2: Effect of multiple IRR

technique needs to be applied in a mutually exclusive basis. However, the IRR can also be misleading when choosing among mutually exclusive projects, that is if the acceptance of any one of them excludes the acceptance of any others. In this case, a project having a greater IRR does not necessarily mean that it will be more profitable. To accurately identify the most profitable investment, the *Incremental rate of return method* (InRR) should be employed. The InRR method (Brealey and Myers, 1988; Stermole and Stermole, 1990) looks at the internal rate of return of the incremental flows (project A minus B or project B minus A, depending on their relative sizes).

For some cases, as Brealey and Myers (1988) argues differences might exist between short-term and long-term interest rates. Thus, it is not clear to which interest rate should the IRR calculated be compared. The presence of several interest rates can also be considered as a possible drawback in the NPV. However, this tool can easily be modified to consider multiple discount rates, as shown in Equation A.10 (Beaves, 1993).

$$NPV = \sum_{n=0}^{Ny} \frac{F_n}{\left(1 + i_{r,n}\right)^n} \tag{A.10}$$

The main criticism against the IRR and probably the most controversial is the implicit reinvestment assumption (Lefley, 1997; Park and Sharp-Bette, 1990; Piekarski, 1991; Ruegg, 1991). This assumption states that the cash flows can be reinvested to earn a return equal to the IRR of the project (Lefley, 1997). Under this assumption, a project that offers a greater return than the cost of capital will be selected, and any surplus funds are reinvested at the IRR of the project. In contrast, in the NPV method the surplus funds are correctly reinvested at the cost of capital (Lefley, 1997). In addition, Ward (1994) argues that the IRR does not accurately measure profitability; since it does not vary with the cost of capital, even though the profitability should increase as the cost of capital decreases. Furthermore, like the NPV, the IRR does not give an indication of the project magnitude (Weaver, 1991).

Two simple variations of the IRR method are also used as a way to compare the IRR calculated against the minimum attractive rate of return. These are the *Internal rate of return index* (IRRI) and the *Internal rate of return margin* (IRRM) that represents the decline that the IRR can take before the project experiences a loss (Morrow, 1991) (see Equations A.11 and A.12)

$$IRRI = \frac{IRR}{i_r} \tag{A.11}$$

$$IRRM = IRR - i_r \tag{A.12}$$

Overall return rate

The overall return rate (ORR)[8] is compared to the minimum attractive rate of return and measures the interest rate that makes the future worth of the cash flows equal the present value of the investments (See Equation A.13) (Ruegg, 1991)

$$\sum_{n=0}^{Ny} F_n (1+i_r)^{Ny-n} = \left[\sum_{m=0}^{Ny} \frac{I_{D,m}}{(1+i_r)^m} \right] (1+ORR)^{Ny} \qquad \text{(A.13)}$$

Solving for ORR,

$$ORR = \left[\frac{\sum_{n=0}^{Ny} F_n (1+i_r)^{Ny-n}}{\sum_{m=0}^{Ny} \frac{I_{D,m}}{(1+i_r)^m}} \right]^{Ny^{-1}} - 1 \qquad \text{(A.14)}$$

The ORR attempts to address the two main drawbacks associated with the IRR tool. First, the existence of multiple rates (Lefley, 1997). Second, the reinvestment assumption. The latter is addressed by assuming that the cash flows are reinvested at the MARR, instead of immediately reinvested at the calculated IRR (Remer and Nieto, 1995a).

As can be seen in Equation A.14, the ORR is easier to calculate than the IRR, since it does not involve a trial and error procedure. However, an apparent disadvantage that still makes the IRR more attractive, is that the ORR needs to be recalculated whenever the discount rate is changed (Piekarski, 1991). In theory, the same disadvantage could be attributed to the NPV method.

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[8] The overall return rate is also known as the external rate of return, growth rate of return, composite rate of return, modified rate of return, adjusted rate of return, and generalized rate of return (Liu and Wu, 1990; Piekarski, 1991; Remer and Nieto, 1995a; Stermole and Stermole, 1990; Ward, 1994).

Discounted payback period

The discounted payback period (DPB), also known as the payout time with interest and net payout time (Jelen, 1970; Remer and Nieto, 1995b; Stermole and Stermole, 1990; Ward, 1994), represents the point in time in which the discounted accumulated cash flows equal zero. In other words, it represents the time required for the project to pay for itself (Remer and Nieto, 1995b).

Given a specified discount rate, the acceptance criterion for this method is generally based upon a minimum required payback period. Furthermore, when comparing among several alternatives the project with the lowest payback period is usually preferred (Remer *et al.*, 1993).

One of the main disadvantages of this technique is that it does not consider the cash flows occurring after the payout period. This can lead to erroneous decisions in project selection. Nevertheless, the DPB represents a quick profitability evaluation tool.

According to Remer *et al.* (1993) there has been a decrease in the use of this method from 78% in 1978 to 64% in 1991. In addition, the survey reports that companies seldom use it by itself. They generally use it in conjunction with either the IRR or the NPV.

Net payout fraction

The net payout fraction (NPF) is to be maximized when comparing alternatives. The NPF is defined as the ratio of the discounted payback period to the operating life (Ward, 1994) (See Equation A.15)

$$NPF = \frac{DPB}{Ny} \tag{A.15}$$

One of the main disadvantages of this technique —like the discounted payback period— is that it does not consider the cash flows occurring after the payout period. This can lead to erroneous decisions in project selection.

Payout period including interest

The payout period including interest (PPI) (Peters and Timmerhaus, 1991) is defined as the ratio of the depreciable investment to the project's average annual profit, without including the investment (see Equation A.16).

$$PPI=\frac{I_D}{\left[\left(\frac{\sum_{n=1}^{Ny}F_n}{(1+i_r)^n}\right)\Big/ Ny\right]} \qquad \text{(A.16)}$$

A.2 NON-TVM METHODS

Cash payback method

The cash payback method (PB)[9] is similar to the DPB method. In this case, the PB estimates the point in time in which the accumulated cash flows equal zero, by considering a discount rate of 0%. Regarding the DPB method, the PB shares the same advantages and disadvantages. However, the use of DPB is preferred since it considers the TVM.

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[9] The cash payback method is also known as the payback method, payback time method, recovery period method, payout period method, payoff period method, payback period, and payout time (Jelen, 1970; Morrow, 1991; Remer and Nieto, 1995b; Stermole and Stermole, 1990).

Payout period

The payout period (PP)[10] of a project, similar to the PPI method, is compared to a minimum time period and it is calculated using Equation A.17 (Peters and Timmerhaus, 1991):

$$P = \frac{I_D}{\left[\left(\sum_{n=1}^{N} F_n\right) Ny^{-1}\right]} \qquad \text{(A.17)}$$

Rate of return on investment

The rate of return on investment (ROR), also known as the return on original investment and average accounting rate of return (Jelen, 1970; Morrow, 1991; Peters and Timmerhaus, 1991), is a variation of the PPI and PP methods. In this case, the ROR —that can be considered as the inverse of the payout period— is compared to the MARR and is calculated as the ratio of the average profit to the total depreciable investment (see Equation A.18

$$ROR = \frac{\left(\sum_{n=0}^{N} F_n\right) N^{-1}}{I_D} \qquad \text{(A.18)}$$

Average return on book value

The average return on book value (ARB)[11] is compared to the MARR and is calculated based on the average annual income and the average annual investment (see Equation A.19

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[10] The payout period of a projects is also known as the payout time, payback period, payoff period, and cash recovery period (Peters and Timmerhaus, 1991).

$$ARB = \frac{\left(\sum_{n=1}^{N} F_n\right) N^{-1}}{\left(\sum_{n=0}^{N} I_D - I_D f_{D,n}\right)(N+1)^{-1}} \tag{A.19}$$

Profit to investment ratio

The profit to investment ratio (PIR), also compared against the MARR, measures the profitability of a project by evaluating the relation between the initial investment and the total undiscounted profit (Remer and Nieto 1995b) (see Equation A.20)

$$PIR = \frac{-I_0 + \sum_{n=1}^{Ny} F_n}{I_0} \tag{A.20}$$

A. 3 COMPARISON STUDY

The economic techniques described previously were evaluated and compared using 13 case studies. The case studies were evaluated on a mutually exclusive basis, that is when comparing one project A against a second project B, the acceptance of the first precludes the acceptance of the second. These examples were taken from different literature sources in an attempt to address the advantages and disadvantages of each method. The examples consider the effect of equal/unequal capital investments, equal/unequal project lives, inflation, taxes, depreciation, interest rate, and negative cash flows in the last years of the project (see Table A.1).

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[11] The Average return on book value is also known as the average book method, average accounting rate of return method, and return on average investment (Brealey and Myers, 1988; Jelen, 1970; Remer and Nieto, 1995b).

Table A.1: Case studies description[12]

Case No.	Reference	Description
1	Ward (1994)	Equal capital investment Unequal lives Equal NPV No inflation
2		Same as case no. 1 with inflation
3	Stermole and Stermole (1990)	Capital investment of project B is 10 times that of project A Equal lives
4	Remer and Nieto (1995a)	Equal Capital Investment Equal lives
5		Same as case no. 4 with $i = 12\%$
6		Same as case no. 4 with $i = 8\%$
7	Ward (1994)	Equal NPV Equal lives
8	Carroll and Newbould (1986)	Negative cash flow in last years of project B
9	Ward (1994)	Equal capital investment Equal lives Equal NPV
10	Ward (1994)	Equal capital investment Equal lives
11		Capital investment of project A is 2 times that of project B NPV values for project A and B similar
12	Ruegg (1991)	Equal capital investment Equal lives
13		Same as case no. 12 with no taxes and inflation

---

[12] The case studies consider (unless otherwise specified): $i_r = 10\%$, $Tx = 34\%$, $i_f = 2\%$.

The economic data for each case (see Table A.2) was used to calculate the values for each of the 19 economic evaluation tools. This was done using a spreadsheet program, that estimates the economic criteria given specific information regarding project lifetime, cash inflows, capital investment, depreciation method, discount rate, and annual inflation rate. The result of this exercise is given in Table A.3, where the best projects selected by the different authors that suggest the comparison examples are included.

The five non-TVM methods in general did not adequately identify the correct process alternatives. Although these methods are easy to calculate, they should be used with caution. In contrast, the TVM methods performed reasonably well with the exception of payout period including interest (PPI) that had problems identifying the correct option, as suggested by the literature sources of each case study.

The internal rate of return (IRR), as discussed previously, can be misleading when comparing between alternatives. This was shown for example in Cases 3, 9, and 10, where the IRR failed in identifying the correct option. However, when the IRR, the internal rate of return index (IRRI), and the internal rate of return margin (IRRM) were evaluated using incremental flows, their behavior was comparable to the NPV. Yet this incremental analysis led to negative flows at the end of the cash flow series. In these circumstances, as happened in Case 8 (see Figure A.2), there exists a possibility of having multiple rates. In this case, as was explained before, the IRR tool should not be employed unless the modified approach suggested by Morrow (1991) is applied. Where, a decision needs to be made as to which discount rate to use in applying this modified approach.

Table A.2: Case studies data

Case No.	Project	Project's income cash flows									
1,2	A	0	-2200	-2400	1600	3500	4000	4000	4000	4000	3800
	B	0	-2200	-2400	900	1300	4500	8100	9238		
3	A	-50	50	50	50	50	50				
	B	-500	250	250	250	250	250				
4,5,6	A	-1000	300	300	300	300	250				
	B	-1000	400	400	300	250	50				
7	A	0	-2200	-2400	1600	3500	4000	4000	4000	4000	3800
	B	0	-3200	-2900	4856	5000	4000	4000	3000	2500	2082
8	A	-770	493	316	133	50	50				
	B	-524	493	316	133	-47	-407				
9	A	0	-2200	-2400	4725	5000	4000	3000	2000	2000	1800
	B	0	-2200	-2400	1130	3000	3000	4000	4000	5000	5800
10	A	0	-2200	-2400	3927	3000	3000	2500	2000	2000	1800
	B	0	-2200	-2400	567	2500	4000	5500	5500	6300	6300
11	A	-1000	325	325	325	330	350				
	B	-500	150	200	200	200	200				
12, 13	A	-100	5	10	10	30	140				
	B	-100	60	30	30	10	10				

Table A.3: Comparison of project evaluation tools

Case	1	2	3	4	5	6	7	8	9	10	11	12	13
	B		**B**	**B**			**A**	**A**	**--**	**B**		**A**	
NPV	--	A	B	B	B	A	--	A	--	B	A	A	A
AEP	B	A	B	B	B	A	--	A	--	B	A	A	A
NRR	B	A	A	B	B	A	A	A	--	B	B	A	A
PI	--	A	A	B	B	A	A	A	--	B	B	A	A
ROR	A	A	A	A	A	A	A	A	B	B	B	A	A
IRR	--	--	A	B	B	B	--	A	A	A	A	A	B
PP	B	B	B	B	B	A	A	B	A	A	A	B	B
PB	B	B	B	A	A	B	B	B	B	B	A	A	A
DPB	B	B	B	A	A	B	B	A	B	B	A	A	A
PPI	--	A	B	A	A	A	A	B	--	A	A	B	B
ARB	B	B	A	A	A	A	A	B	B	B	B	A	A
ORR	--	A	A	B	B	A	A	A	--	B	B	A	A
PWP	--	A	A	B	B	A	A	A	--	B	B	A	A
FW	--	A	B	B	B	A	--	A	--	B	A	A	A
NPF	A	B	B	A	A	A	A	A	B	B	A	A	A
PIR	A	A	A	A	A	A	A	A	B	B	B	A	A
IRRI	--	--	A	B	B	B	--	A	A	A	B	A	B
IRRM	--	--	A	B	B	B	--	A	A	A	B	A	B
InRR	--	A	B	B	B	B	--	A	--	B	A	A	A

Regarding the multiple rates, the overall rate of return (ORR) successfully selected the alternatives that the IRR failed to identify. However, the ORR, like the IRR and NPV presented difficulties when evaluating unequal initial investments. That is, when comparing between alternatives, one project can have an investment several times that of the other. However, this difference might not be reflected when the IRR, NPV or ORR is calculated. For example, Case 11 considered that project's A capital investment was two times that of project B. The NPV calculated for project A and B was \$131 and \$126 respectively. Hence, the NPV does not consider the need to invest twice as much to get a similar return. In this example, the net return rate (NRR) was successful in identifying this behavior. Apparently, as suggested by Ward (1994) the NRR is the answer to the unequal investment dilemma. However, in Case 3 project B requires ten times more capital investment to obtain five times more net profit. Therefore, is it worth investing in project B? According to the NRR apparently not. However, if the total amount of capital —$ 500 — is available for investment, the company would be better off investing it in project B than obtaining the corresponding return based on the MARR.

Case 1 represented an interesting example, since most methods remained indifferent regarding a particular project. This example is given by Ward (1994) where the cash flows of each project are varied in order to obtain equal NPV on both alternatives. Ward (1994) argues that the NPV failed to identify the correct project. However, when the chain rule is applied to consider projects with unequal lives, the NPV and FW selected the correct method; as the AEP did without the use of this chain rule. Yet, as discussed previously, when two projects are replicated a crossover point might exist, where there is a possibility of a reversal in the ranking of projects. Therefore one might argue on the benefits of applying the annual equivalent profit, but as Ancel and Griffiths (1996) demonstrate for some instances the use of the AEP method incorrectly identifies the best option when dealing with different project lives.

Finally, the evaluation tool is not the only economic variable that can affect the ranking of the investment options. Other circumstances that might impact such ranking is the choice of the different economic parameters, such as the inflation rate (see Case 1 and 2) and the MARR (see Case 4 and 6).

APPENDIX B

HIDDEN COSTS EXPENSES SPECIFIC DATA

Table B.1: Data to be used in calculating hidden cost expenses[1]

Cost item	Status #[2]	Description	f_H	m_H	t	s
Notification						
RCRA	3	Exportation of hazardous waste notification	1	2	2-3	25
	6; 7	RCRA foreign source notification	0-5	1	2	20
	6	RCRA permit confirmation	1-4	1	2	20
	6; 7	Local notification of operations	1	3	40	25
	6; 7	Manifest discrepancy notification	0-125	1	2	25
SARA	9; 10	Facility changes notification	1-5	1	8	25
	9; 10	Emergency follow-up notification	0-2	1	8-16	25
	12	Supplier notification requirements	0-2	1	2	9
CAA	13	Startup, monitoring and operations change notifications				
	14	Hazardous emissions test notification	1	1	1	25
CWA	15	NPDES discharge notification				
	17	Hazardous pollutant discharge notification				
	18	Toxic pollutant discharge notification[3]				
	16	Industrial user slug loading notification				
OSHA	22; 23	Material safety data sheets	0.4-8	1	0.25	9
Reporting						
RCRA	1; 2	Generators biennial report	0.5	5	8	25
	1	LQG exception report	0.1-1.5	1	2	25
	2	SQG exception report	0-0.1	1	0.25	25
	3	Primary exporters exception report	0.1-1.5	1	2	25
	6; 7	TSDF biennial report	0-125	1	1	25
	6; 7	TSDF unmanifested waste report	0-125	1	1	25

---

[1] This table presents a summary of the information contained in EPA (1989). Unless otherwise specified, the data was taken from this source and assumed to be represented in 1989 dollars.. Several cost items do not have present estimate values. For this case, the requirements are generally specific to the site, process, or operation.

[2] For a description of the status numbers see Table B.2

[3] This requirement applies only to six chemicals for which effluent standards have been promulgated: aldrin/dieldrin, DDT and metabolites, endrin and metabolites, polychlorinated buphenyls (PCBs), and toxaphene.

Table B.1: Data to be used in calculating hidden cost expenses *(Continued)*

Cost item	Status #	Description	f_H	m_H	*t*	*s*
	6; 7	Release, fire, explosion, and closure reporting	2	2	5	25
SARA	11	Supplemental MSDS report	0.04-8	4	0.5	20
	11	Requested MSDS report		1	0.25	20
	11	Inventory report	1	1	5	25
	11	Tier II reporting by request	0-1	1	5	25
	12	Excess of applicable threshold report	1	1	8-40	25
CAA	13	Quarterly compliance and monitoring assessment report	4	2	5	25
	13	Performance test results reporting	4	2	2	25
	13	Opacity test results reporting	4	2	2	25
	14	Hazardous pollutant emissions reporting	1	2	8	25
	14	Hazardous pollutant monitoring system reporting	2	1	5	25
CWA	15	NPDES Permit reporting requirements				
	16	Industrial users' continued compliance report	2	2	5	25
	18	Toxic standards annual compliance report[4]	1-6	1	5	25
OSHA	20	Injury and illness reporting each occurrence	0.05-5	1	1.5	20
	20	Injury and illness annual summary	1	0.25	1	20
	19; 20	Fatality or hospitalization report	.005-0.5	0	1-10	20
	19; 20	Occupational injuries and illness survey	1-2	0	0.5-3	20
Monitoring/ testing						
RCRA	6; 7	Hazardous waste chemical and physical analysis				
	6	Groundwater monitoring				
	7	Groundwater monitoring/land-based				
CAA	13	Emissions control performance testing				
	13	Continuous monitoring system				
	13	Continuous opacity monitoring system				

---

[4] See footnote 3.

Table B.1: Data to be used in calculating hidden cost expenses *(Continued)*

Cost item	**Status #**	**Description**	f_H	m_H	t	s
	14	Hazardous pollutant testing				
	14	Hazardous pollutant monitoring				
CWA	15	Effluent stream monitoring and sampling				
	16	Pretreatment standards monitoring				
	18	Daily toxic pollutant sampling				
Recordkeeping						
RCRA	1; 2	Exports, test results & waste analysis records	5-100	1	0.25	9
	3	Exporter's reports and notifications records	5	1	0.25	9
	5	Manifesting records	0-200	1	0.25	9
	6; 7	Operating record	250	1	0.25	9
SARA	12	Excess of threshold reports and documentation	0-2	1	1	9
	12	Notification determination records	0-2	1	1	9
CAA	13	Startup, shutdown and malfunctioning records	10	1	1	9
	13	Performance test data records	4	1	0.25	9
	13	Opacity test data record	4	1	0.25	9
	14	Hazardous pollutant monitoring data records	4	1	1	9
	14	Hazardous emissions test results records	4	1	1	9
CWA	15	NPDES monitoring records				
	16	Industrial users/POTW pretreatment records				
	18	Toxic pollutant effluent discharge compliance records				
OSHA	19; 20	Occupational injuries and illness log and summary	1-5	3	0.25	9
	23	Medical surveillance program records				

Table B.1: Data to be used in calculating hidden cost expenses *(Continued)*

Cost item	**Status #**	**Description**	f_H	m_H	t	s
Planning/ Studies/ Modeling						
RCRA	6	Final status TSDF detection monitoring program				
	7	Ground-water outline of TSDFs				
	6	Final status TSDF compliance monitoring program				
	6; 7	Emergency & contingency plan procedures				
	6; 7	Cost estimate for facility closure				
OSHA	22	Hazard communication program				
	23	Safety and health program				
	23	Emergency response program				
Training						
RCRA	2	SQG emergency response coordinator				
	2	SQG waste handling & emergency planning				
	6; 7	Personnel training				
	6; 7	TSDF emergency response coordinator training				
OSHA	22; 23	Initial assignment and addition of hazard training				
	23	Hazardous waste training				
Inspections						
RCRA	6	Facility inspection and inspection schedule				
	1 & 4	LQG tank inspections				
	2 & 4	SQG tank inspections				
SARA	11	Fire department inventory inspections				
CAA	13	Point source inspections				
CWA	15	Compliance inspections				
Manifesting						
RCRA	1; 2	Generators off-site transport manifesting	4-100	0.5	0.25-1	25
	5	Transporter shipment manifest	4-500	0.5	1-3	15-25
	6; 7	TSDF standard manifesting	4-500	0.5	0.25-1	25

Table B.1: Data to be used in calculating hidden cost expenses *(Continued)*

Cost item	**Status #**	**Description**	f_H	m_H	t	s
Labeling						
RCRA	1; 2	Pre-Transportation Labeling	4-500	2	0.25	15
	1; 2	Hazardous waste package marking	4-500	2	0.25	15
	1; 2	Transporter placarding	4-500	15	0.25	15
OSHA	22	Hazardous chemical labeling				
Preparedness/ protective equipment[5]						
RCRA	6; 7	Internal communicating alarm system, fire control equipment, etc.				
CWA	15	NPDES backup or auxiliary facilities				
OSHA	21	Restricted exposure to certain chemicals				
Closure/Post closure assurance						
RCRA	6	Final assurance for closure and post closure				
Medical surveillance						
OSHA	23	Hazardous waste medical surveillance program				
Insurance and special taxes						
RCRA		Financial responsibility requirements				
CERCLA		Taxes on certain chemicals				
Other						

---

[5] Estimates for personal protective equipment are presented in Stillman (1993).

Table B.2: Regulatory status numbers used in Table B.1

Status #	**Description**
1	RCRA large quantity generator (LQG)
2	RCRA small quantity generator (SQG)
3	Primary exporter of hazardous waste
4	Hazardous waste storage tanks
5	Transport of hazardous waste
6	Final status TSD facility
7	Interim status TSD facility
8	Use CERCLA section 4661 chemicals
9	Handle any 40 CFR Section 355 Appendix A and B extremely hazardous substances at or above their Title III threshold
10	Occasionally release reportable quantities of CERCLA hazardous substances or any extremely hazardous substances
11	Maintain any material safety data sheets
12	Have 10 or more employees and fall within SIC codes 2000 to 3999 and within the year handle 40 CFR section 372.65 toxic chemicals above thresholds stated in 40 CFR section 372.25
13	A new stationary source
14	Emit hazardous air pollutants
15	Discharge wastewaters directly to surface water
16	Discharge wastewaters to a POTW
17	Occasionally discharge reportable quantities of hazardous substances as defined in 40 CFR §117
18	Have toxic pollutant discharges for which chemical-specific standards have been promulgated
19	Have less than 10 employees or falls within SIC codes 52-89 (excluding 52-54, 70, 75, 76, 79, 80)
20	Have 10 or more employees and does not fall within SIC codes 52-89 (excluding 52-54, 70, 75, 76, 79, 80)
21	Have OSHA air contaminants as per 29 CFR §1910.100
22	Handle any hazardous chemicals as defined in 29 CFR §1910.1200(c)
23	A hazardous waste TSDF, or a LQG of hazardous waste, or a facility accumulation of hazardous wastes for 90 or more days

APPENDIX C

EXPERIMENTAL DESIGN ANALYSIS EXAMPLE

APPENDIX C

EXPERIMENTAL DESIGN ANALYSIS EXAMPLE

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EXPERIMENTAL DESIGN ANALYSIS EXAMPLE

ratio, and their corresponding lower and upper values are 750/900, 15/20, and 150/800 respectively. For a full factorial design 2^3, the design matrix and the contrast coefficient table is given in Table C.3.

The temperature effect in Table C.3 is calculated by multiplying the *T* column times the response column (CH_3Cl) and dividing by the respective divider (see Equation C.1)

$$T = \frac{-49.4 + 55.2 - 36.1 + 31.5 - 49.6 + 55.3 - 31.5 + 28.8}{4} = 1.04 \qquad \text{(C.1)}$$

In a similar manner, the effects of the remaining variables can be calculated. And as can be seen in Table C.3, the variables having the most important effect on the amount of methyl chloride produced are the chlorine flowrate and the reaction temperature. The latter is identified as a response from its interaction with the chlorine flowrate (Column T-M).

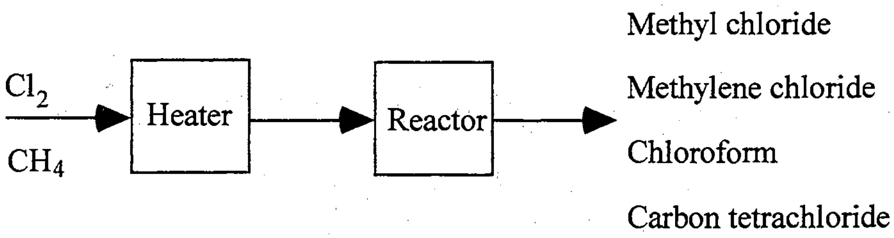

Figure C.1: Reactor system for the manufacture of methyl chloride

Table C.3: Design and response matrix for the analysis of the methyl chloride reactor system[1]

Exp	Average	T	M	P	T-M	T-P	M-P	T-M-P	CH_3Cl	Avg.	T	M	P	T-M	T-P	M-P	T-M-P
1	1	-1	-1	-1	1	1	1	-1	49.4	49.4	-49	-49	-49	49	49	49	-49
2	1	1	-1	-1	-1	-1	1	1	55.2	55.2	55	-55	-55	-55	-55	55	55
3	1	-1	1	-1	-1	1	-1	1	36.1	36.1	-36	36	-36	-36	36	-36	36
4	1	1	1	-1	1	-1	-1	-1	31.5	31.5	32	32	-32	32	-32	-32	-32
5	1	-1	-1	1	1	-1	-1	1	49.6	49.6	-50	-50	50	50	-50	-50	50
6	1	1	-1	1	-1	1	-1	-1	55.3	55.3	55	-55	55	-55	55	-55	-55
7	1	-1	1	1	-1	-1	1	-1	31.5	31.5	-31	31	31	-31	-31	31	-31
8	1	1	1	1	1	1	1	1	28.8	28.8	29	29	29	29	29	29	29
Divider	8	4	4	4	4	4	4	4		42.2	1.04	-20	-1.8	-4.7	0.44	-1.9	0.51

---

[1] The initials in Table C.3, T, M, and P correspond to the three variables evaluated, that is the reactor temperature, the chlorine mole flow, and the reactor presssure respectively. The shaded region corresponds to the design matrix.

APPENDIX D

STOCHASTIC ANNEALING OPTIMIZATION FOR THE METHYL CHLORIDE REACTOR SYSTEM

```
TITLE 'OPTIMIZATION STUDY FOR STOCHASTIC ANNEALING ALGORITHM'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

DIAGNOSTICS
    TERMINAL SIM-LEVEL=0 CONV-LEVEL=0 COST-LEVEL=0 PROP-LEVEL=0 &
        ECON-LEVEL=0 STREAM-LEVEL=0 SYS-LEVEL=0

DESCRIPTION "
        THIS RUN INCLUDES THE OPTIMIZATION OF THE REACTION
        FOR THE PRODUCTION OF METHYL CHLORIDE, THROUGH THE
        THERMAL CHLORINATION OF METHANE. IN THIS CASE, THE
        STOCHASTIC ANNEALING METHOD WILL BE USED. "

DATABANKS AQUEOUS   / ASPENPCD  / PURECOMP  / SOLIDS   /   &
        INORGANIC

PROP-SOURCES AQUEOUS   / ASPENPCD   / PURECOMP   / SOLIDS   /   &
        INORGANIC

COMPONENTS
    HCL HCL HCL /
    CL2 CL2 CL2 /
    CH4 CH4 CH4 /
    CH3CL CH3CL CH3CL /
    CH2CL2 CH2CL2 CH2CL2 /
    CHCL3 CHCL3 CHCL3 /
    CCL4 CCL4 CCL4

FLOWSHEET
    BLOCK B1 IN=RAW OUT=6
    BLOCK B2 IN=6 OUT=5
    BLOCK B3 IN=3 OUT=7
    BLOCK HX1 IN=5 OUT=2
    BLOCK R1 IN=2 OUT=3

PROPERTIES NRTL-RK

STREAM RAW
    SUBSTREAM MIXED TEMP=77.0 PRES=14.70
    MOLE-FLOW CL2 600 / CH4 280.0

BLOCK B1 HEATER
    PARAM TEMP=77.0 PRES=0.0

BLOCK B2 HEATER
    PARAM TEMP=77.0 PRES=14.70

BLOCK B3 HEATER
    PARAM TEMP=77.0 PRES=14.70
```

```
BLOCK HX1 HEATER
    PARAM TEMP=572.0 PRES=0.0

BLOCK R1 RCSTR
    PARAM VOL=1600.0 TEMP=842.0 PRES=0.0
    REACTIONS RXN-IDS=RSCH-1

FORTRAN CONTROL
; *****************************************************
;  For each optimization variable, Xi, two parameters
;  need to be specified: (1) the specific variable X1 and
;  (2) a place to store its old value X1OLD using a
;  parameter description.
;  For the uncertain parameters, if they are flowsheet
;  variables they just need to be sampled.  However, if
;  they represent an external variable such as a product
;  price, they need to be specified also under the
;  parameter description
; *****************************************************
F      COMMON /RAND/ IX, IY, IIZ
F      COMMON /CONT/ LOOP, LOOP2, ICK, IN, IN2, ACC, ICK2
F      COMMON /ANNEAL/ T, TLEV, ALFA, EMOBJ, ML, QOBJ, QCNT
F      COMMON /STAT/ SAMP, NSAMP, OBJ(1000), RES(500)
F      COMMON /STOP/ TOL
    DEFINE U1 PARAMETER 1
    DEFINE X1OLD PARAMETER 2
    DEFINE T3 BLOCK-VAR BLOCK=B3 VARIABLE=TEMP   &
         SENTENCE=PARAM
    DEFINE X1 BLOCK-VAR BLOCK=R1 VARIABLE=TEMP   &
         SENTENCE=PARAM
    DEFINE X2 MOLE-FLOW STREAM=RAW SUBSTREAM=MIXED  &
        COMPONENT=CL2
    DEFINE X2OLD PARAMETER 3
F      WRITE(NTERM,*) 'T,ALFA,TLEVEL',T,ALFA,TLEV
F      IF (ICK .EQ. 1) THEN
F         LOOP2=LOOP2+1
C      ** CHECK WHETER EQUILIBRIUM HAS BEEN REACHED **
F         IF ((LOOP2 .GT. ML) .OR. (ACC .GT. 10)) GOTO 40
F         T3=T3+0.1*LOOP2
F         WRITE(NTERM,*) 'T3',T3
C      ** DETERMINATION OF RANDOM NUMBER OF SAMPLES **
F 25        R=RDM()
F           IF (R .LE. 0.5) S=SAMP-5*RDM()
F           IF (R .GT. 0.5) S=SAMP+5*RDM()
F           IF (S .LT. 2) GOTO 25
F           SAMP=S
F           NSAMP=IDINT(SAMP)
F           WRITE(NTERM,*) 'NSAMP',NSAMP
C      ** NEW VALUES FOR OPTIMIZATION VARIABLES **
F           X1OLD=X1
F 15        X1=X1+(2*RDM()-1)*10
C          ** SET LIMITS TO OPTIMIZATION VARIABLE **
F           IF ((X1 .LT. 750) .OR. (X1 .GT. 900)) GOTO 15
F           X2OLD=X2
```

```
F 18        X2=X2+(2*RDM()-1)*10
C          ** SET LIMITS TO OPTIMIZATION VARIABLE **
F           IF ((X2 .LT. 150) .OR. (X2 .GT. 800)) GOTO 18
F           WRITE(NTERM,*) 'LOP2 VDF: X1,X2 ',LOOP2,X1,X2
F           ICK=0
F           LOOP=0
F           IF (IN .EQ. 0) T3=77
F      END IF
C      ** SAMPLING OF UNCERTAIN PARAMETERS **
F      U1=RDM()*(1.1-0.9)+0.9
F      WRITE(NTERM,*) 'U1: ',U1
F      GOTO 50
F 40   T=T*ALFA
F      RES(TLEV)=EMOBJ
F      TLEV=TLEV+1
F      ACC=0
F      RRR=ABS(EMOBJ-QOBJ)
F      IF (RRR .LT. TOL) THEN
F         QCNT=QCNT+1
F         WRITE(NTERM,*) 'QCNT',QCNT
F      ELSE
F         QCNT=0
F         QOBJ=EMOBJ
F      END IF
F      IF (QCNT .LE. 5) THEN
F         LOOP2=0
F         T3=77.0
F      END IF
F      IF (QCNT .GT. 5) THEN
F         DO 45 I=1,TLEV-1
F            WRITE(NTERM,*) I,RES(I)
F 45      CONTINUE
F         LOOP2=0
F      END IF
F      WRITE(NTERM,*) 'EQUIL REACHED',T,TLEV
F 50   IN=0
    EXECUTE AFTER BLOCK B2

FORTRAN INIT
F      COMMON /RAND/ IX, IY, IIZ
F      COMMON /CONT/ LOOP, LOOP2, ICK, IN, IN2, ACC, ICK2
F      COMMON /ANNEAL/ T, TLEV, ALFA, EMOBJ, ML, QOBJ, QCNT
F      COMMON /STAT/ SAMP, NSAMP, OBJ(1000), RES(500)
F      COMMON /STOP/ TOL
    DEFINE T3 BLOCK-VAR BLOCK=B3 VARIABLE=TEMP
       SENTENCE=PARAM
C   ** READ SEED NUMBERS REQUIRED FOR RANDOM FUNCTION RDM()**
F      WRITE (NTERM,*) 'RANDOM SEED NUMBER (IX) ?'
F      READ (NTERM,*) IX
F      WRITE (NTERM,*) 'RANDOM SEED NUMBER (IY) ?'
F      READ (NTERM,*) IY
F      WRITE (NTERM,*) 'RANDOM SEED NUMBER (IZ) ?'
F      READ (NTERM,*) IIZ
C   ** INITIALIZE CONTROL VARIABLES **
```

```
F     LOOP2=0
F     ICK=1
F     TLEV=1.0
F     IN=1
F     IN2=1
F     ICK2=1
F     QCNT=0
F     ACC=0
C      ***********************************
C      INITIALIZE USER SPECIFIED VARIABLES
C      SAMP = initial sample size
C     T = initial temperature
C      ML = Markov chain length
C     ***********************************
F     TOL=0.1
F     SAMP=5
F     T=25
F     ALFA=0.9
F     ML=30
    EXECUTE FIRST

FORTRAN STOCH
F     COMMON /RAND/ IX, IY, IIZ
F     COMMON /CONT/ LOOP, LOOP2, ICK, IN, IN2, ACC, ICK2
F     COMMON /ANNEAL/ T, TLEV, ALFA, EMOBJ, ML, QOBJ, QCNT
F     COMMON /STAT/ SAMP, NSAMP, OBJ(1000), RES(500)
    DEFINE CH3 MOLE-FLOW STREAM=3 SUBSTREAM=MIXED  &
        COMPONENT=CH3CL
    DEFINE U1 PARAMETER 1
    DEFINE X1OLD PARAMETER 2
    DEFINE T3 BLOCK-VAR BLOCK=B3 VARIABLE=TEMP   &
         SENTENCE=PARAM
    DEFINE X1 BLOCK-VAR BLOCK=R1 VARIABLE=TEMP   &
         SENTENCE=PARAM
    DEFINE X2 MOLE-FLOW STREAM=RAW SUBSTREAM=MIXED  &
        COMPONENT=CL2
    DEFINE X2OLD PARAMETER 3
F     IF (ICK2 .EQ. 1) GOTO 50
F     IF (LOOP2 .EQ. 0) GOTO 50
F     LOOP=LOOP+1
F     IF (LOOP .LT. NSAMP+1) T3=T3+0.1*(LOOP+LOOP2)
F     WRITE(NTERM,*) 'T3',T3
C  ** CALCULATION OF OBJECTIVE FUNCTION **
F     OBJ(LOOP)=-CH3*U1
F     WRITE(NTERM,*) 'LOOP: OBJ FUNCTION',LOOP, OBJ(LOOP)
C  ** STATISTICS **
F     IF (LOOP .EQ. NSAMP) THEN
F        SUMA=0
F        SUMS=0
C     ** OBJECTIVE FUNCTION AVERAGE **
F        DO 10 I=1,NSAMP
F          SUMA=SUMA+OBJ(I)
F          WRITE(NTERM,*) 'STAT OBJ FUNC',I,OBJ(I)
F 10     CONTINUE
```

```
F        EVNOBJ=SUMA/NSAMP
C     ** OBJECTIVE FUNCTION STANDARD DEVIATION **
F        DO 20 I=1,NSAMP
F           SUMS=SUMS+(OBJ(I)-EVNOBJ)**2
F 20     CONTINUE
F        SDEV=DSQRT(SUMS/(NSAMP-1))
F        WRITE(NTERM,*) 'AVERAGE & SDEV',EVNOBJ,SDEV
F        ICK=1
C     ** GENERATE THE WEIGHTING FUNCTION **
F        BT=0.001/(0.9**TLEV)
C     ** CALCULATE NEW OBJECTIVE FUNCTION **
F        EMNOBJ=EVNOBJ+2*BT*SDEV/(NSAMP**0.5)
F        IF (IN2 .EQ. 1) THEN
F           IN2=0
F           EMOBJ=EMNOBJ
F           GOTO 50
F        END IF
F        DELTA=EMNOBJ-EMOBJ
F        IF (DELTA .LT. 0) GOTO 30
F        W=DEXP(-DELTA/T)
F        WRITE (NTERM,*) 'DEXP',W
F        IF (W .GT. RDM()) GOTO 30
C     ** REJECT THE MOVE **
F        X1=X1OLD
F        X2=X2OLD
F        WRITE(NTERM,*) 'REJ: X1,X2,EMOBJ,CS',X1,X2,EMOBJ,CS
F        GOTO 50
C     ** ACCEPT THE MOVE **
F 30     EMOBJ=EMNOBJ
F        ACC=ACC+1
F        CS=EVNOBJ
F        WRITE(NTERM,*) 'ACC',ACC
F        WRITE(NTERM,*) 'ACT: X1,X2,EMOBJ,CS',X1,X2,EMOBJ,CS
F     END IF
F 50  ICK2=0
    EXECUTE BEFORE BLOCK B3

TRANSFER T-1
    SET BLOCK-VAR BLOCK=B1 VARIABLE=TEMP SENTENCE=PARAM
    EQUAL-TO BLOCK-VAR BLOCK=B3 VARIABLE=TEMP SENTENCE=PARAM


CONVERGENCE C-1 DIRECT
    TEAR 6
    PARAM MAXIT=9999

SEQUENCE S-1 INIT C-1 B2 CONTROL HX1 R1 STOCH B3 T-1 B1  &
        (RETURN C-1)

REACTIONS RSCH-1 POWERLAW
    REAC-DATA 1 PHASE=V CBASIS=MOLARITY
    REAC-DATA 2 PHASE=V CBASIS=MOLARITY
    REAC-DATA 3 PHASE=V CBASIS=MOLARITY
    REAC-DATA 4 PHASE=V CBASIS=MOLARITY
```

```
RATE-CON 1 PRE-EXP=256000000.0 ACT-ENERGY=35260.0
RATE-CON 2 PRE-EXP=62800000.0 ACT-ENERGY=30580.0
RATE-CON 3 PRE-EXP=256000000.0 ACT-ENERGY=35260.0
RATE-CON 4 PRE-EXP=293000000.0 ACT-ENERGY=37490.0
STOIC 1 MIXED CH4 -1.0 / CL2 -1.0 / CH3CL 1.0 / HCL  &
    1.0
STOIC 2 MIXED CH3CL -1.0 / CL2 -1.0 / CH2CL2 1.0 /  &
    HCL 1.0
STOIC 3 MIXED CH2CL2 -1.0 / CL2 -1.0 / CHCL3 1.0 /  &
    HCL 1.0
STOIC 4 MIXED CHCL3 -1.0 / CL2 -1.0 / CCL4 1.0 / HCL  &
    1.0
POWLAW-EXP 1 MIXED CH4 1.0 / MIXED CL2 1.0
POWLAW-EXP 2 MIXED CH3CL 1.0 / MIXED CL2 1.0
POWLAW-EXP 3 MIXED CH2CL2 1.0 / MIXED CL2 1.0
POWLAW-EXP 4 MIXED CHCL3 1.0 / MIXED CL2 1.0
```

APPENDIX E

RANDOM NUMBER GENERATOR SUBROUTINE

```
C -----------------------------------------------------------
C              RANDOM NUMBER GENERATOR
C
C   The algorithm taken from Wichmann and Hill (1985)
C   returns a pseudo-random number rectangularly distributed
C   between 0 and 1
C
C   The random seed numbers IX, IY, and IIZ* need to be
C   declared as integers and set to a value from 1 to 30000
C   for the first iteration
C
C   The subroutine's object file should be present in the
C   ASPEN PLUS working directory or in the directory where
C   the input file is located.
C
C   *Note: To avoid conflicts with ASPEN PLUS, variables
C          starting with IZ cannot be used.
C -----------------------------------------------------------

      FUNCTION RDM ()

C     Each FORTRAN block that calls for the random number
C     function must contain the following common block.

      COMMON /RAND/ IX, IY, IIZ

        IX=171*MOD(IX,177)-2*(IX/177)
        IY=172*MOD(IY,176)-35*(IY/176)
        IIZ=170*MOD(IIZ,178)-63*(IIZ/178)

        IF (IX .LT. 0) IX=IX+30269
        IF (IY .LT. 0) IY=IY+30307
        IF (IIZ .LT. 0) IIZ=IIZ+30323

        RDM=AMOD(FLOAT(IX)/30269.0+FLOAT(IY)/30307.0+
     2     FLOAT(IIZ)/3023.0,1.0)

        RETURN
        END
```

APPENDIX F

BASE CASE MODEL INPUT FILE

```
TITLE 'Methyl Chloride Base Case Model'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

DATABANKS ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        PURECOMP

PROP-SOURCES ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC /  &
        PURECOMP

COMPONENTS
    H2O H2O H2O /
    CH4 CH4 CH4 /
    NAOH NAOH NAOH /
    NA+ NA+ NA+ /
    H3O+ H3O+ H3O+ /
    "NAOH(S)" NAOH "NAOH(S)" /
    OH- OH- OH- /
    CL2 CL2 CL2 /
    HCL HCL HCL /
    CH3CL CH3CL CH3CL /
    CH2CL2 CH2CL2 CH2CL2 /
    CHCL3 CHCL3 CHCL3 /
    CCL4 CCL4 CCL4 /
    HCLO HCLO HCLO /
    "NACL(S)" NACL "NACL(S)" /
    CLO- CLO- CLO- /
    CL- CL- CL- /
    H2SO4 H2SO4 H2SO4 /
    HSO4- HSO4- HSO4- /
    SO4-- SO4-2 SO4-- /
    N2 N2 N2

HENRY-COMPS ABS-DRY CL2 HCLO HCL CH4 CH3CL CH2CL2 CHCL3 CCL4

CHEMISTRY ABS
    STOIC 1 H2O -2 / H3O+ 1 / OH- 1
    STOIC 2 HCL -1 / H2O -1 / H3O+ 1 / CL- 1
    STOIC 3 CL2 -1 / H2O -2 / HCLO 1 / H3O+ 1 / CL- 1
    STOIC 4 HCLO -1 / H2O -1 / CLO- 1 / H3O+ 1
    K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0
    K-STOIC 3 A=-11.37532 B=-1286.972 C=0 D=0
    K-STOIC 4 A=-16.1519 B=-1602.87 C=0 D=0

CHEMISTRY DRY1
    DISS NAOH NA+ 1 / OH- 1
    STOIC 1 H2O -2 / H3O+ 1 / OH- 1
    STOIC 2 HCL -1 / H2O -1 / H3O+ 1 / CL- 1
    STOIC 3 CL2 -1 / H2O -2 / HCLO 1 / H3O+ 1 / CL- 1
    STOIC 4 HCLO -1 / H2O -1 / CLO- 1 / H3O+ 1
    K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0
    K-STOIC 3 A=-11.37532 B=-1286.972 C=0 D=0
```

```
    K-STOIC 4 A=-16.1519 B=-1602.87 C=0 D=0
    SALT "NACL(S)" NA+ 1 / CL- 1
    SALT "NAOH(S)" NA+ 1 / OH- 1
    K-SALT "NACL(S)" A=-203.5875 B=4381.176 C=35.87518  &
        D=-.06721607

CHEMISTRY DRY2
    STOIC 1 H2O -2 / H3O+ 1 / OH- 1
    STOIC 2 H2SO4 -1 / H2O -1 / H3O+ 1 / HSO4- 1
    STOIC 3 HSO4- -1 / H2O -1 / H3O+ 1 / SO4-- 1
    K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0

FLOWSHEET
    BLOCK DR1 IN=NAOH 5 OUT=6 W3
    BLOCK DR2 IN=H2SO4 7 OUT=8 W4
    BLOCK HX3 IN=6 OUT=7
    BLOCK ABS IN=H2O 4 OUT=5 W2
    BLOCK CMP1 IN=8 OUT=9
    BLOCK HX4 IN=9 OUT=10
    BLOCK FL1 IN=10 OUT=11 12
    BLOCK HX2 IN=3 OUT=4
    BLOCK D1 IN=12 OUT=15 13
    BLOCK D2 IN=13 OUT=CH2CL2 14
    BLOCK D3 IN=14 OUT=CHCL3 W5
    BLOCK MX1 IN=CH4 CL2 19 OUT=1
    BLOCK CSTR IN=2 OUT=3
    BLOCK HX1 IN=1 OUT=2
    BLOCK CMP2 IN=18 OUT=19
    BLOCK SPL IN=17 OUT=WPRG 18
    BLOCK FL2 IN=15 OUT=16 CH3CL
    BLOCK MX2 IN=16 11 OUT=17

PROPERTIES NRTL-RK
    PROPERTIES ELECNRTL

PROP-DATA HENRY-1
    IN-UNITS ENG PRESSURE='N/SQM' TEMPERATURE=K PDROP=PSI
    PROP-LIST HENRY
    BPVAL CL2 H2O 169.5452000 -9487.196000 -20.812340 0.0  &
        273.0000000 400.0000000
    BPVAL HCL H2O 58.45296000 -7762.832000 0.0 0.0 273.00  &
        400.0000000
    BPVAL HCLO H2O -20.000000 0.0 0.0 0.0 273.0000000  &
        400.000000
    BPVAL CH2CL2 H2O 29.104 -3817.0 0.0 0.0 283.0 308.0
    BPVAL CHCL3 H2O 32.294 -4612 0.0 0.0 283.0 308.0
    BPVAL CCL4 H2O 33.741 -4411.0 0.0 0.0 283.0 308.0
    BPVAL CH4 H2O 195.2940000 -9111.670000 -25.03790000  &
        1.43434000E-4 275.0000000 353.0000000
    BPVAL CH3CL H2O 184.0280000 -9768.6200 -23.42400 0.0  &
        277.0000000 353.0000000

PROP-DATA NRTL-1
    IN-UNITS ENG
```

```
    PROP-LIST NRTL
    BPVAL H2O HCLO 11.25094000 0.0 .3000000 0.0 0.0 0.0  &
        32.00000407 211.9999993
    BPVAL HCLO H2O -7.175849000 0.0 .3000000 0.0 0.0 0.0  &
        32.00000407 211.9999993

PROP-DATA VLCLK-1
    IN-UNITS ENG
    PROP-LIST VLCLK
    BPVAL NA+ OH- -.2209618842 1.168080748
    BPVAL NA+ CL- .2425544521 .4050617606
    BPVAL H3O+ CL- .5534556818 .2140997348
    BPVAL NA+ SO4-- .1389686094 1.974549497
    BPVAL H3O+ HSO4- .8778750527 .3242692779

PROP-DATA GMELCC-1
    IN-UNITS ENG
    PROP-LIST GMELCC
    PPVAL H2O ( NA+ OH- ) 6.737997000
    PPVAL ( NA+ OH- ) H2O -3.771221000
    PPVAL H2O ( NA+ CL- ) 5.980196000
    PPVAL ( NA+ CL- ) H2O -3.789168000
    PPVAL H2O ( NA+ HSO4- ) 7.663000000
    PPVAL ( NA+ HSO4- ) H2O -3.944000000
    PPVAL H2O ( NA+ SO4-- ) 7.689221000
    PPVAL ( NA+ SO4-- ) H2O -4.284786000
    PPVAL H2O ( H3O+ OH- ) 8.045000000
    PPVAL ( H3O+ OH- ) H2O -4.072000000
    PPVAL H2O ( H3O+ CL- ) 4.110129000
    PPVAL ( H3O+ CL- ) H2O -3.344103000
    PPVAL H2O ( H3O+ HSO4- ) 6.362000000
    PPVAL ( H3O+ HSO4- ) H2O -3.749000000
    PPVAL H2O ( H3O+ SO4-- ) 8.000000000
    PPVAL ( H3O+ SO4-- ) H2O -4.000000000
    PPVAL CL2 ( NA+ OH- ) 15.00000000
    PPVAL ( NA+ OH- ) CL2 -8.000000000
    PPVAL CL2 ( NA+ CLO- ) 15.00000000
    PPVAL ( NA+ CLO- ) CL2 -8.000000000
    PPVAL CL2 ( NA+ CL- ) 15.00000000
    PPVAL ( NA+ CL- ) CL2 -8.000000000
    PPVAL CL2 ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) CL2 -8.000000000
    PPVAL CL2 ( H3O+ CLO- ) 15.00000000
    PPVAL ( H3O+ CLO- ) CL2 -8.000000000
    PPVAL CL2 ( H3O+ CL- ) 15.00000000
    PPVAL ( H3O+ CL- ) CL2 -8.000000000
    PPVAL HCL ( NA+ OH- ) 15.00000000
    PPVAL ( NA+ OH- ) HCL -8.000000000
    PPVAL HCL ( NA+ CLO- ) 15.00000000
    PPVAL ( NA+ CLO- ) HCL -8.000000000
    PPVAL HCL ( NA+ CL- ) 15.00000000
    PPVAL ( NA+ CL- ) HCL -8.000000000
    PPVAL HCL ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) HCL -8.000000000
```

```
        PPVAL HCL ( H3O+ CLO- ) 15.00000000
        PPVAL ( H3O+ CLO- ) HCL -8.000000000
        PPVAL HCL ( H3O+ CL- ) 12.00000000
        PPVAL ( H3O+ CL- ) HCL -1.0000000E-3
        PPVAL HCL ( H3O+ HSO4- ) 10.00000000
        PPVAL ( H3O+ HSO4- ) HCL -2.000000000
        PPVAL HCL ( H3O+ SO4-- ) 15.00000000
        PPVAL ( H3O+ SO4-- ) HCL -8.000000000
        PPVAL HCLO ( NA+ OH- ) 15.00000000
        PPVAL ( NA+ OH- ) HCLO -8.000000000
        PPVAL HCLO ( NA+ CLO- ) 15.00000000
        PPVAL ( NA+ CLO- ) HCLO -8.000000000
        PPVAL HCLO ( NA+ CL- ) 15.00000000
        PPVAL ( NA+ CL- ) HCLO -8.000000000
        PPVAL HCLO ( H3O+ OH- ) 15.00000000
        PPVAL ( H3O+ OH- ) HCLO -8.000000000
        PPVAL HCLO ( H3O+ CLO- ) 15.00000000
        PPVAL ( H3O+ CLO- ) HCLO -8.000000000
        PPVAL HCLO ( H3O+ CL- ) 15.00000000
        PPVAL ( H3O+ CL- ) HCLO -8.000000000
        PPVAL H2SO4 ( H3O+ CL- ) 10.00000000
        PPVAL ( H3O+ CL- ) H2SO4 -2.000000000
        PPVAL H2SO4 ( H3O+ HSO4- ) 12.99200000
        PPVAL ( H3O+ HSO4- ) H2SO4 -2.981000000
        PPVAL H2SO4 ( H3O+ SO4-- ) 8.000000000
        PPVAL ( H3O+ SO4-- ) H2SO4 -4.000000000
        PPVAL ( NA+ OH- ) ( NA+ CL- ) 8.407678000
        PPVAL ( NA+ CL- ) ( NA+ OH- ) 1.950440000
        PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 3.147792000
        PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -.5387706000
        PPVAL ( NA+ CL- ) ( NA+ SO4-- ) -11.44869000
        PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -.2697454000
        PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) .9536271000
        PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0

    PROP-DATA GMELCD-1
        IN-UNITS ENG
        PROP-LIST GMELCD
        PPVAL H2O ( NA+ OH- ) 2556.435478
        PPVAL ( NA+ OH- ) H2O -849.2763195
        PPVAL H2O ( NA+ CL- ) 1514.732508
        PPVAL ( NA+ CL- ) H2O -389.4562614
        PPVAL H2O ( NA+ SO4-- ) 1018.076891
        PPVAL ( NA+ SO4-- ) H2O -102.3078191
        PPVAL H2O ( H3O+ CL- ) 4151.955402
        PPVAL ( H3O+ CL- ) H2O -1176.370324
        PPVAL H2O ( H3O+ HSO4- ) 3524.759832
        PPVAL ( H3O+ HSO4- ) H2O -1049.759950
        PPVAL H2O ( H3O+ SO4-- ) 0.0
        PPVAL ( H3O+ SO4-- ) H2O 0.0
        PPVAL CL2 ( NA+ OH- ) 0.0
        PPVAL ( NA+ OH- ) CL2 0.0
        PPVAL CL2 ( NA+ CLO- ) 0.0
        PPVAL ( NA+ CLO- ) CL2 0.0
```

```
    PPVAL CL2 ( NA+ CL- ) 0.0
    PPVAL ( NA+ CL- ) CL2 0.0
    PPVAL CL2 ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) CL2 0.0
    PPVAL CL2 ( H3O+ CLO- ) 0.0
    PPVAL ( H3O+ CLO- ) CL2 0.0
    PPVAL CL2 ( H3O+ CL- ) 0.0
    PPVAL ( H3O+ CL- ) CL2 0.0
    PPVAL HCL ( NA+ OH- ) 0.0
    PPVAL ( NA+ OH- ) HCL 0.0
    PPVAL HCL ( NA+ CLO- ) 0.0
    PPVAL ( NA+ CLO- ) HCL 0.0
    PPVAL HCL ( NA+ CL- ) 0.0
    PPVAL ( NA+ CL- ) HCL 0.0
    PPVAL HCL ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) HCL 0.0
    PPVAL HCL ( H3O+ CLO- ) 0.0
    PPVAL ( H3O+ CLO- ) HCL 0.0
    PPVAL HCL ( H3O+ CL- ) 0.0
    PPVAL ( H3O+ CL- ) HCL 0.0
    PPVAL HCL ( H3O+ HSO4- ) 0.0
    PPVAL ( H3O+ HSO4- ) HCL 0.0
    PPVAL HCL ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) HCL 0.0
    PPVAL HCLO ( NA+ OH- ) 0.0
    PPVAL ( NA+ OH- ) HCLO 0.0
    PPVAL HCLO ( NA+ CLO- ) 0.0
    PPVAL ( NA+ CLO- ) HCLO 0.0
    PPVAL HCLO ( NA+ CL- ) 0.0
    PPVAL ( NA+ CL- ) HCLO 0.0
    PPVAL HCLO ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) HCLO 0.0
    PPVAL HCLO ( H3O+ CLO- ) 0.0
    PPVAL ( H3O+ CLO- ) HCLO 0.0
    PPVAL HCLO ( H3O+ CL- ) 0.0
    PPVAL ( H3O+ CL- ) HCLO 0.0
    PPVAL H2SO4 ( H3O+ HSO4- ) -3119.219851
    PPVAL ( H3O+ HSO4- ) H2SO4 -292.1399861
    PPVAL H2SO4 ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) H2SO4 0.0
    PPVAL ( NA+ OH- ) ( NA+ CL- ) -324.8080045
    PPVAL ( NA+ CL- ) ( NA+ OH- ) -1491.716269
    PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 1408.793693
    PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -170.8229619
    PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 6763.469077
    PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -240.5010485
    PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) -363.1438627
    PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0

PROP-DATA GMELCE-1
    IN-UNITS ENG
    PROP-LIST GMELCE
    PPVAL H2O ( NA+ OH- ) 3.013932000
    PPVAL ( NA+ OH- ) H2O 2.136557000
```

```
PPVAL H2O ( NA+ CL- ) 7.433500000
PPVAL ( NA+ CL- ) H2O -1.100418000
PPVAL H2O ( NA+ SO4-- ) -14.08276000
PPVAL ( NA+ SO4-- ) H2O 8.547499000
PPVAL H2O ( H3O+ CL- ) .3417959000
PPVAL ( H3O+ CL- ) H2O 2.121453000
PPVAL H2O ( H3O+ HSO4- ) -4.599000000
PPVAL ( H3O+ HSO4- ) H2O 4.472000000
PPVAL CL2 ( NA+ OH- ) 0.0
PPVAL ( NA+ OH- ) CL2 0.0
PPVAL CL2 ( NA+ CLO- ) 0.0
PPVAL ( NA+ CLO- ) CL2 0.0
PPVAL CL2 ( NA+ CL- ) 0.0
PPVAL ( NA+ CL- ) CL2 0.0
PPVAL CL2 ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) CL2 0.0
PPVAL CL2 ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) CL2 0.0
PPVAL CL2 ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) CL2 0.0
PPVAL HCL ( NA+ OH- ) 0.0
PPVAL ( NA+ OH- ) HCL 0.0
PPVAL HCL ( NA+ CLO- ) 0.0
PPVAL ( NA+ CLO- ) HCL 0.0
PPVAL HCL ( NA+ CL- ) 0.0
PPVAL ( NA+ CL- ) HCL 0.0
PPVAL HCL ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) HCL 0.0
PPVAL HCL ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) HCL 0.0
PPVAL HCL ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) HCL 0.0
PPVAL HCL ( H3O+ SO4-- ) 0.0
PPVAL ( H3O+ SO4-- ) HCL 0.0
PPVAL HCLO ( NA+ OH- ) 0.0
PPVAL ( NA+ OH- ) HCLO 0.0
PPVAL HCLO ( NA+ CLO- ) 0.0
PPVAL ( NA+ CLO- ) HCLO 0.0
PPVAL HCLO ( NA+ CL- ) 0.0
PPVAL ( NA+ CL- ) HCLO 0.0
PPVAL HCLO ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) HCLO 0.0
PPVAL HCLO ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) HCLO 0.0
PPVAL HCLO ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) HCLO 0.0
PPVAL H2SO4 ( H3O+ HSO4- ) -30.12600000
PPVAL ( H3O+ HSO4- ) H2SO4 .8060000000
PPVAL ( NA+ OH- ) ( NA+ CL- ) 100.0000000
PPVAL ( NA+ CL- ) ( NA+ OH- ) 6.619543000
PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 43.39265000
PPVAL ( NA+ SO4-- ) ( NA+ OH- ) 4.518955000
PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 60.25378000
PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -4.302999000
```

```
PROP-DATA GMELCN-1
    IN-UNITS ENG
    PROP-LIST GMELCN
    PPVAL H2O ( NA+ OH- ) .2000000000
    PPVAL H2O ( NA+ CL- ) .2000000000
    PPVAL H2O ( NA+ SO4-- ) .2000000000
    PPVAL H2O ( H3O+ HSO4- ) .2000000000
    PPVAL CL2 ( NA+ OH- ) .1000000000
    PPVAL CL2 ( NA+ CLO- ) .1000000000
    PPVAL CL2 ( NA+ CL- ) .1000000000
    PPVAL CL2 ( H3O+ OH- ) .1000000000
    PPVAL CL2 ( H3O+ CLO- ) .1000000000
    PPVAL CL2 ( H3O+ CL- ) .1000000000
    PPVAL HCL ( NA+ OH- ) .1000000000
    PPVAL HCL ( NA+ CLO- ) .1000000000
    PPVAL HCL ( NA+ CL- ) .1000000000
    PPVAL HCL ( H3O+ OH- ) .1000000000
    PPVAL HCL ( H3O+ CLO- ) .1000000000
    PPVAL HCL ( H3O+ SO4-- ) .1000000000
    PPVAL HCLO ( NA+ OH- ) .1000000000
    PPVAL HCLO ( NA+ CLO- ) .1000000000
    PPVAL HCLO ( NA+ CL- ) .1000000000
    PPVAL HCLO ( H3O+ OH- ) .1000000000
    PPVAL HCLO ( H3O+ CLO- ) .1000000000
    PPVAL HCLO ( H3O+ CL- ) .1000000000
    PPVAL H2SO4 ( H3O+ HSO4- ) .2000000000

STREAM CH4
    SUBSTREAM MIXED TEMP=77 PRES=14.7 MOLE-FLOW=323
    MOLE-FRAC CH4 0.98 / N2 0.02

STREAM CL2
    SUBSTREAM MIXED TEMP=77 PRES=14.7
    MOLE-FLOW CL2 320

STREAM H2O
    SUBSTREAM MIXED TEMP=90 PRES=14.7
    MOLE-FLOW H2O 2025

STREAM H2SO4
    SUBSTREAM MIXED TEMP=77 PRES=14.7 MOLE-FLOW=200
    MOLE-FRAC H2SO4 1

STREAM NAOH
    SUBSTREAM MIXED TEMP=86 PRES=14.7 NPHASE=1 PHASE=S
    MOLE-FLOW NAOH 200

BLOCK MX1 MIXER

BLOCK MX2 MIXER

BLOCK SPL FSPLIT
    FRAC WPRG 0.1
```

```
BLOCK HX1 HEATER
    PARAM TEMP=572 PRES=0

BLOCK HX2 HEATER
    PARAM TEMP=100 PRES=0

BLOCK HX3 HEATER
    PARAM TEMP=100 PRES=0

BLOCK HX4 HEATER
    PARAM TEMP=-58 PRES=0

BLOCK FL1 FLASH2
    PARAM PRES=0 DUTY=0

BLOCK FL2 FLASH2
    PARAM TEMP=-100 PRES=0

BLOCK D3 DSTWU
    PARAM LIGHTKEY=CHCL3 RECOVL=0.999 HEAVYKEY=CCL4  &
        RECOVH=0.001 PTOP=14.7 PBOT=14.7 NSTAGE=10

BLOCK ABS RADFRAC
    PARAM NSTAGE=2
    FEEDS H2O 1 ON-STAGE / 4 2 ON-STAGE
    PRODUCTS 5 1 V / W2 2 L
    P-SPEC 1 14.7
    COL-SPECS Q1=0 QN=0 MOLE-RDV=1
    PROPERTIES ELECNRTL HENRY-COMPS=ABS-DRY CHEMISTRY=ABS  &
        TRUE-COMPS=NO

BLOCK D1 RADFRAC
    PARAM NSTAGE=12
    FEEDS 12 6
    PRODUCTS 13 12 L / 15 1 V
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RDV=1 MOLE-RR=1.2
    SPEC 1 MOLE-RECOV 0.995 COMPS=CH3CL STREAMS=15
    VARY 1 D:F 0.001 0.999

BLOCK D2 RADFRAC
    PARAM NSTAGE=20
    FEEDS 13 10
    PRODUCTS CH2CL2 1 L / 14 20 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RDV=0 MOLE-RR=1.5
    SPEC 1 MOLE-RECOV 0.999 COMPS=CH2CL2 STREAMS=CH2CL2
    VARY 1 D:F 0.001 0.999

BLOCK DR1 RADFRAC
    PARAM NSTAGE=5 MAXOL=30
    FEEDS NAOH 1 ON-STAGE / 5 5 ON-STAGE
    PRODUCTS 6 1 V / W3 5 L
```

```
    P-SPEC 1 14.7
    COL-SPECS Q1=0 QN=0 MOLE-RDV=1
    T-EST 1 400 / 2 300
    X-EST 1 NAOH 0.9 / 1 H2O 0.1 / 1 CL2 0 / 1 HCL 0
    Y-EST 1 NAOH 0 / 1 H2O 0.2 / 1 CL2 0 / 1 HCL 0
    PROPERTIES ELECNRTL HENRY-COMPS=ABS-DRY CHEMISTRY=DRY1 &
        TRUE-COMPS=NO

BLOCK DR2 RADFRAC
    PARAM NSTAGE=2
    FEEDS H2SO4 1 ON-STAGE / 7 2 ON-STAGE
    PRODUCTS 8 1 V / W4 2 L
    P-SPEC 1 14.7
    COL-SPECS Q1=0 QN=0 MOLE-RDV=1
    PROPERTIES ELECNRTL HENRY-COMPS=ABS-DRY CHEMISTRY=DRY2 &
        TRUE-COMPS=NO

BLOCK CSTR RCSTR
    PARAM VOL=1600 TEMP=525 <C> PRES=0
    REACTIONS RXN-IDS=RSCH-1

BLOCK CMP2 COMPR
    PARAM TYPE=ASME-POLYTROP DELP=45

BLOCK CMP1 COMPR
    PARAM TYPE=ASME-POLYTROP PRES=115 TEMP=275

DESIGN-SPEC DS-1
    DEFINE H2O MOLE-FRAC STREAM=8 SUBSTREAM=MIXED COMPONENT=H2O
    SPEC "H2O" TO "0.00003"
    TOL-SPEC "0.00002"
    VARY MOLE-FLOW STREAM=H2SO4 SUBSTREAM=MIXED COMPONENT=H2SO4
    LIMITS "200" "500"

REACTIONS RSCH-1 POWERLAW
    REAC-DATA 1 PHASE=V
    REAC-DATA 2 PHASE=V
    REAC-DATA 3 PHASE=V
    REAC-DATA 4 PHASE=V
    RATE-CON 1 PRE-EXP=2.56E8 ACT-ENERGY=35260
    RATE-CON 2 PRE-EXP=6.28E7 ACT-ENERGY=30580
    RATE-CON 3 PRE-EXP=2.56E8 ACT-ENERGY=35260
    RATE-CON 4 PRE-EXP=2.93E8 ACT-ENERGY=37490
    STOIC 1 MIXED CH4 -1 / CL2 -1 / CH3CL 1 / HCL 1
    STOIC 2 MIXED CH3CL -1 / CL2 -1 / CH2CL2 1 / HCL 1
    STOIC 3 MIXED CH2CL2 -1 / CL2 -1 / CHCL3 1 / HCL 1
    STOIC 4 MIXED CHCL3 -1 / CL2 -1 / CCL4 1 / HCL 1
    POWLAW-EXP 1 MIXED CH4 1 / MIXED CL2 1
    POWLAW-EXP 2 MIXED CH3CL 1 / MIXED CL2 1
    POWLAW-EXP 3 MIXED CH2CL2 1 / MIXED CL2 1
    POWLAW-EXP 4 MIXED CHCL3 1 / MIXED CL2 1
```

APPENDIX G

SUPPORT DATA FOR METHYL CHLORIDE PROCESS ANALYSIS

Table G.1: Characterization of process streams[1]

Type	Stream ID	Source	Destination	State	Quantity (kg/hr)	Composition (wt%)	
F	CH4	-	MX1	Vapor	2,386	CH_4	0.98
						N_2	0.02
F	Cl2	-	MX1	Vapor	10,292	Cl_2	1.00
F	H2O	-	ABS	Liquid	16,548	H_2O	1.00
F	NAOH	-	DR1	Solid	3,628	NaOH	1.00
F	H2SO4	-	DR2	Liquid	13,551	H_2SO_4	1.00
I	1	MX1	HX1	Vapor	19,187	Cl_2	0.54
						CH_4	0.39
						N_2	0.04
						CH_3Cl	0.03
						CH_2Cl_2	≈ 0
						$CHCl_3$	≈ 0
I	3	CSTR	MX1	Vapor	19,187	CH_4	0.31
						HCl	0.27
						CH_3Cl	0.22
						CH_2Cl_2	0.11
						N_2	0.04
						$CHCl_3$	0.04
						Cl_2	< 0.01
						CCl_4	< 0.01
I	8	DR2	CMP1	Vapor	13,793	CH_4	0.43
						CH_3Cl	0.31
						CH_2Cl_2	0.15
						N_2	0.06
						$CHCl_3$	0.05
						CCl_4	0.01
						H_2O	≈ 0
						H_2SO_4	≈ 0

---

[1] Stream type: F=feed, I=intermediate, P=product, R=recycle, and W=waste.

Table G.1: Characterization of process streams (*Continued*)

Type	Stream ID	Source	Destination	State	Quantity (kg/hr)	Composition (wt%)	
I	12	FL1	D1	Liquid	7,014	CH_3Cl	0.54
						CH_2Cl_2	0.28
						$CHCl_3$	0.10
						CH_4	0.06
						CCl_4	0.02
						N_2	< 0.01
						H_2O	≈ 0
						H_2SO_4	≈ 0
P	CH3CL	FL2	-	Liquid	3,716	CH_3Cl	0.99
						CH_4	0.01
						N_2	≈ 0
P	CH2CL2	D2	-	Liquid	2,130	CH_2Cl_2	0.94
						$CHCl_3$	0.06
						CH_3Cl	< 0.01
P	CHCL3	D3	-	Liquid	579	$CHCl_3$	0.99
						CH_2Cl_2	< 0.01
P	W5	D3	-	Liquid	135	CCl_4	0.99
						H_2O	< 0.01
						$CHCl_3$	< 0.01
						H_2SO_4	< 0.01
R	17	MX2	SPL	Vapor	7,233	CH_4	0.81
						CH_3Cl	0.08
						N_2	0.11
						CH_2Cl_2	< 0.01
W	W2	ABS	-	Liquid	18,746	H_2O	0.72
						HCl	0.27
						CH_3Cl	< 0.01
						CH_2Cl_2	< 0.01
						N_2	< 0.01

Table G.1: Characterization of process streams (*Continued*)

Type	Stream ID	Source	Destination	State	Quantity (kg/hr)	Composition (wt%)	
W	W3	DR1	-	Liquid	4,758	NaOH	0.76
						H_2O	0.18
						Cl_2	0.04
						HCl	0.01
W	W4	DR2	-	Liquid	15,618	H_2SO_4	0.87
						H_2O	0.13
						CH_3Cl	≈ 0
W	WPRG	SPL	-	Vapor	723	CH_4	0.81
						CH_3Cl	0.08
						N_2	0.11
						CH_2Cl_2	< 0.01

Table G.2: Environmental impact of process chemicals[2]

Chemical	Regulatory status and environmental impact
Methylene chloride	• Included in the 33/50 voluntary reduction program • Hazardous air pollutant • RCRA hazardous waste #U080 • RCRA land ban waste • EPA list of priority pollutants • SARA section 313 toxic chemicals • Carcinogen
Chloroform	• Included in the 33/50 voluntary reduction program • Hazardous air pollutant • CWA hazardous substance • RCRA land ban waste • EPA list of priority pollutants • SARA section 313 toxic chemicals • Carcinogen • RCRA hazardous waste #U044
Carbon tetrachloride	• Included in the 33/50 voluntary reduction program • Hazardous air pollutant • CWA hazardous substance • RCRA land ban waste • EPA list of priority pollutants • RCRA hazardous waste #U211 • SARA section 313 toxic chemicals • According to the Montreal Protocol[3] fugitive emission need to be eliminated by the year 2000 and a production ban went into effect in 1996.
Chlorine	• Corrosive • Hazardous air pollutant • CWA hazardous substance • Suspect carcinogen, mutagen, or reproductive hazard • SARA section 313 toxic chemicals • Extremely hazardous waste • Acutely hazardous material

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[2] Most of the information presented in this table is based on Stanford University's Chemical Safety Database (avaialble on-line at http://www-portfolio.stanford.edu/100369) and on the summary given by Pohanish (1997).

[3] The Montreal Protocol is an international agreement that went into effect in 1987 designed to achieve eventual elimination of certain fluorocarbons and chorofluorocarbons (Lamprecht, 1997).

Table G.2: Environmental impact of process chemicals *(Continued)*

Chemical	Regulatory status and environmental impact
Sulfuric acid	• Hazardous air pollutant • Suspect carcinogen, mutagen, or reproductive hazard • SARA section 313 toxic chemicals • Acutely hazardous material • Corrosive
Methane	• CAA Accidental release prevention/flammable substance
Sodium hydroxide	• Corrosive • CWA hazardous substance • SARA section 313 toxic chemicals
Hydrogen chloride	• Suspect carcinogen, mutagen, or reproductive hazard • SARA section 313 toxic chemicals • Extremely hazardous waste • Acutely hazardous material • Corrosive
Methyl chloride	• Hazardous air pollutant • RCRA hazardous waste #U045 • RCRA land ban waste • EPA list of priority pollutants • SARA section 313 toxic chemicals • Suspect carcinogen, mutagen, or reproductive hazard

Table G.3: Economic data for base case[4]

Raw materials / solvents / products	
Chlorine	0.28 \$/kg
Methane (includes cryogenic purification)	0.16 \$/kg
Process water	0.00044 \$/kg
Sulfuric acid	0.083 \$/kg
Sodium hydroxide	3.75 \$/kg
Methyl chloride	0.85 \$/kg
Methylene chloride	0.95 \$/kg
Chloroform	0.66 \$/kg
Carbon tetrachloride	0.79 \$/kg
Hydrogen chloride	0.14 \$/kg
Utilities	
Cooling water	6.87×10^{-6} \$/kg
Chilled water	2.96×10^{-5} \$/kg
Low pressure steam	0.0054 \$/kg
High pressure steam	0.01 \$/kg
Electricity	0.035 \$/kwh

---

[4] The prices for the raw materials, solvents, and products were taken from the CMR (1998). For the case of methane, since a high purity feed is required, its price will depend upon the characteristics of the natural gas source and the operating conditions of the purification process. Therefore, the quoted price for natural gas was increased to reflect the cost associated with the separation and purification of methane through cryogenics, based on estimated manufacturing costs given by Jordan (1972) (A more up to date study of natural gas processing is given by Diaz *et al.* (1997). However, the economics presented by these authors is not clearly defined and was therefore not included in the base case economic model). The remaining expenses associated with the utilities were estimated using the scaling factors suggested by Douglas (1988) based on the quoted ratefor electricity. With respect to the refrigeration system, it was taken as a triple stage ethylene/propylene system capable of delivering the required temperatures (GPSA, 1994).

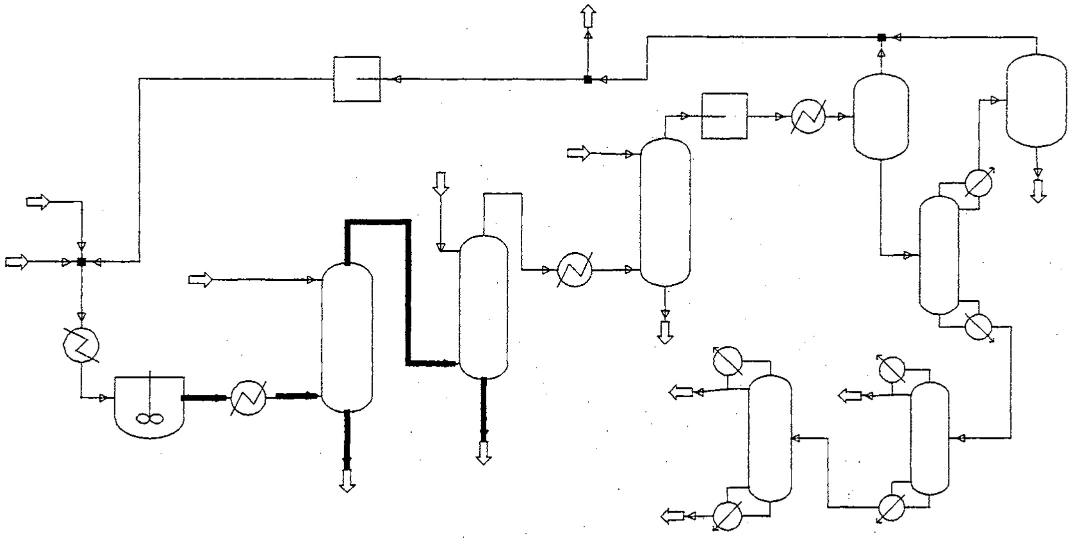

Figure G.1: Hydrogen chloride SFC

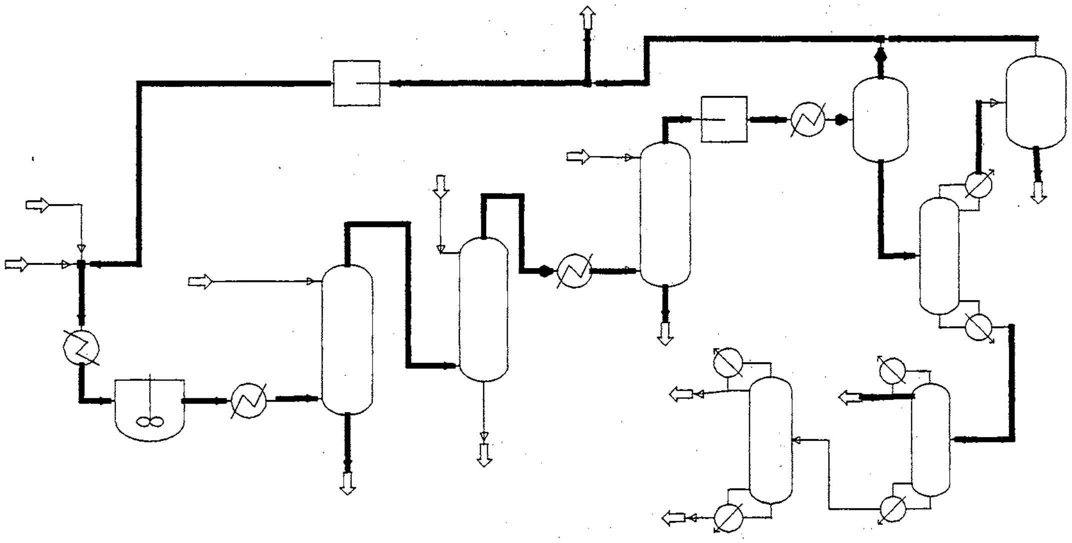

Figure G.2: Methyl chloride SFC

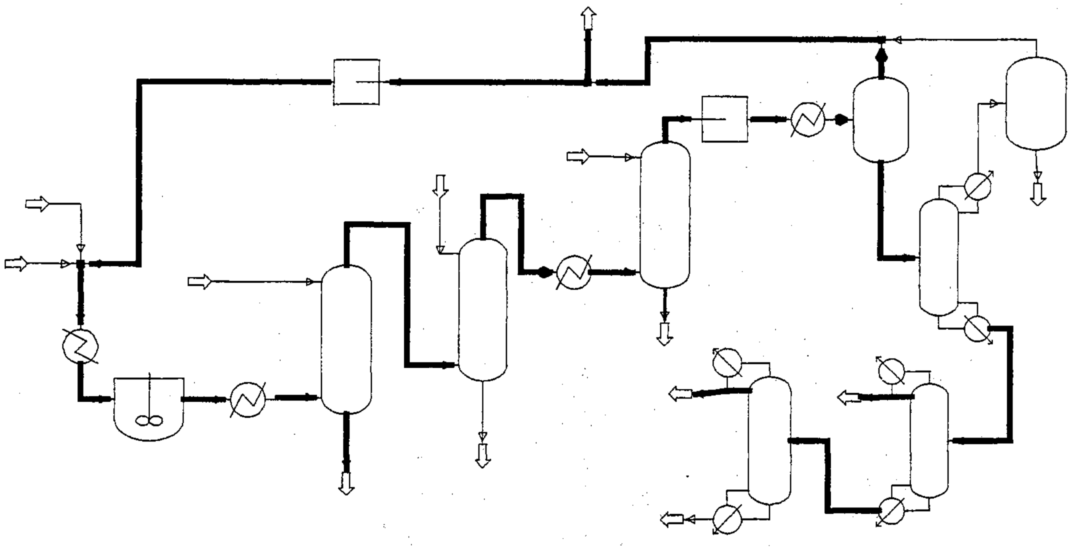

Figure G.3: Methylene chloride SFC

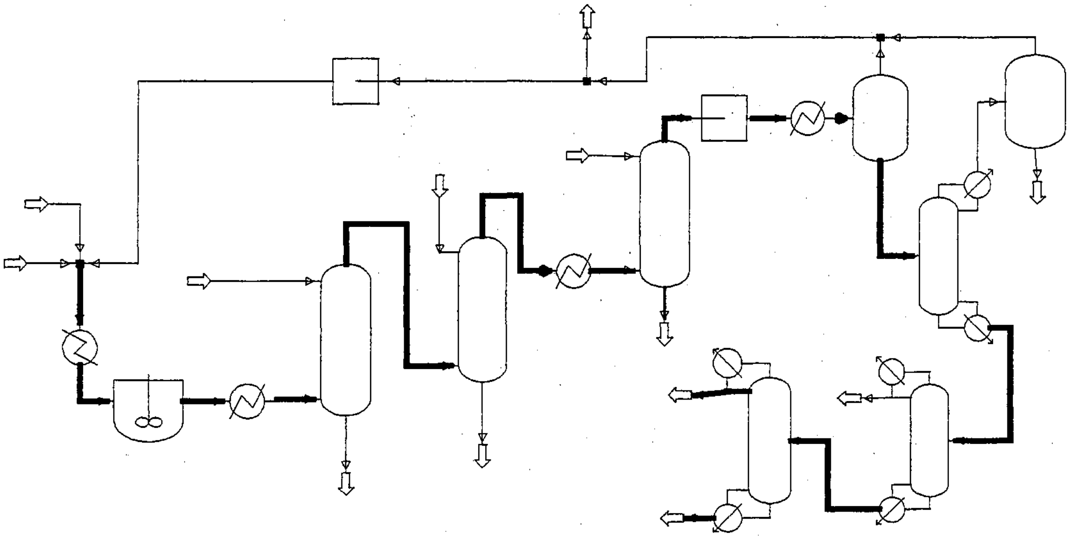

Figure G.4: Chloroform SFC

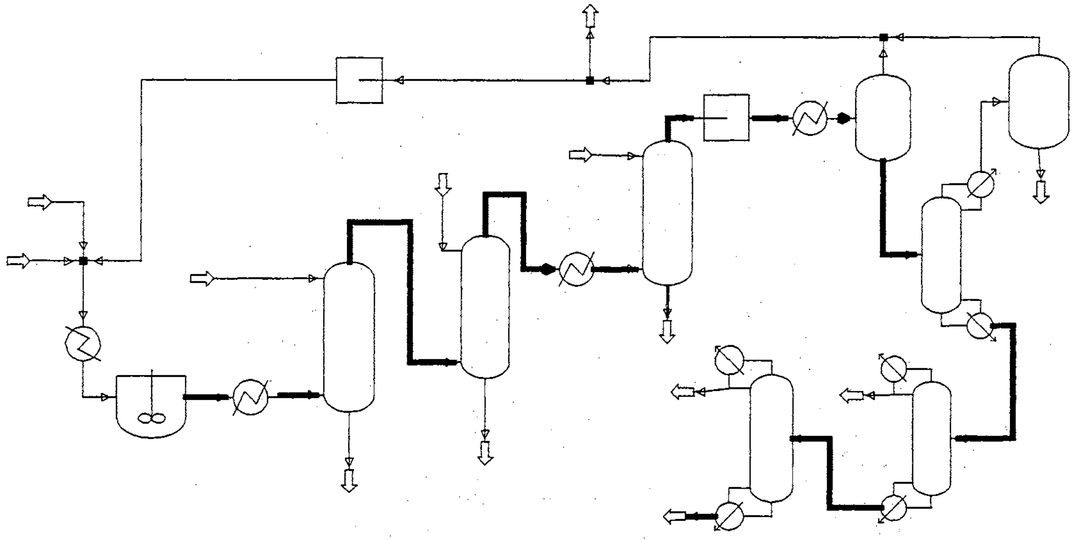

Figure G.5: Carbon tetrachloride SFC

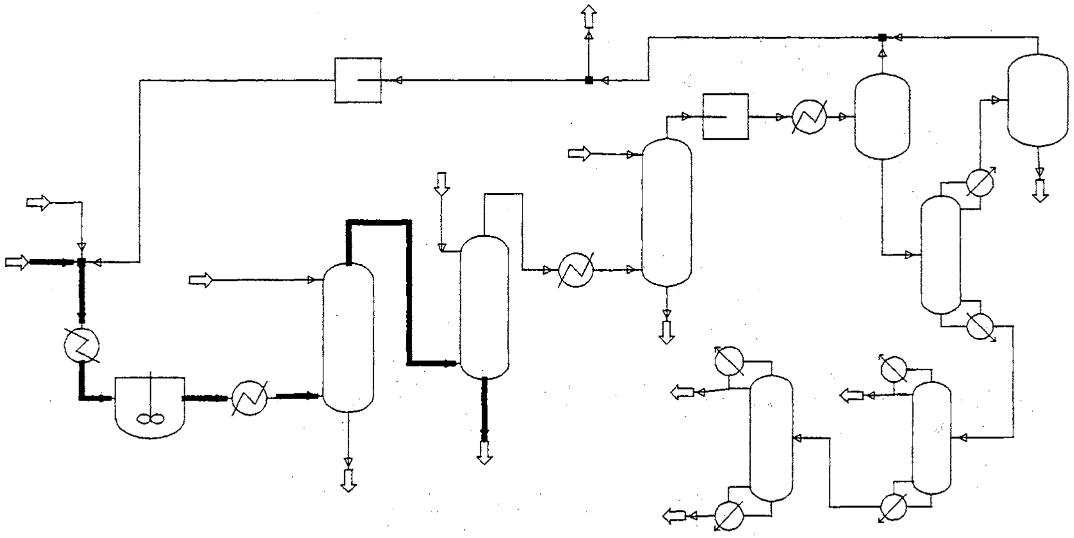

Figure G.6: Chlorine SFC

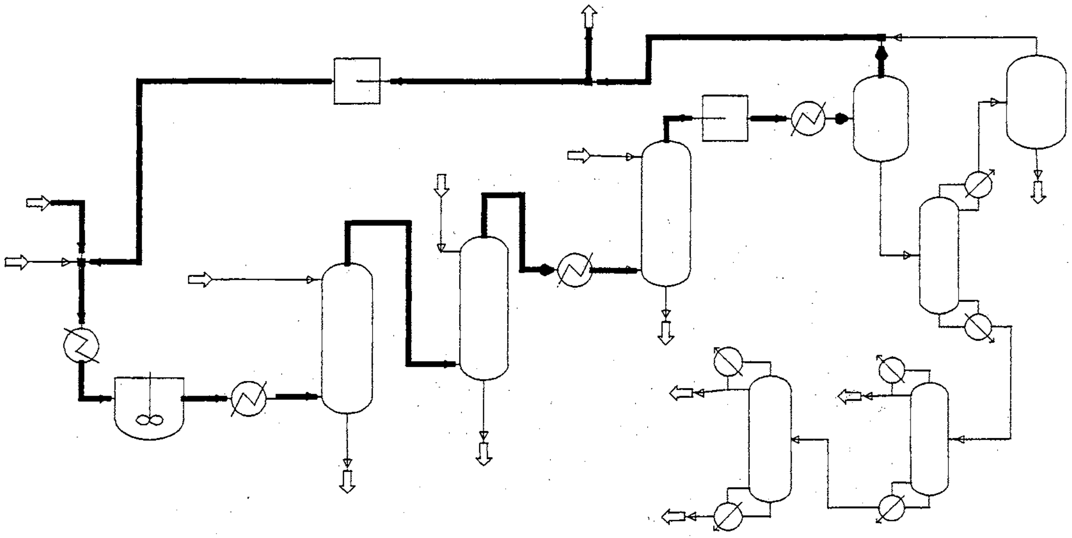

Figure G.7: Methane SFC

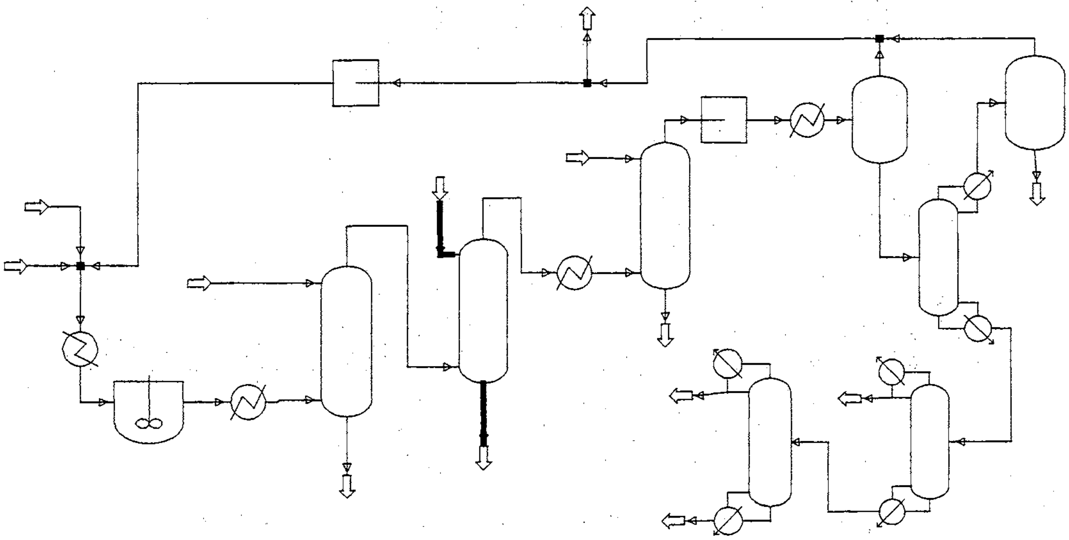

Figure G.8: Sodium hydroxide SFC

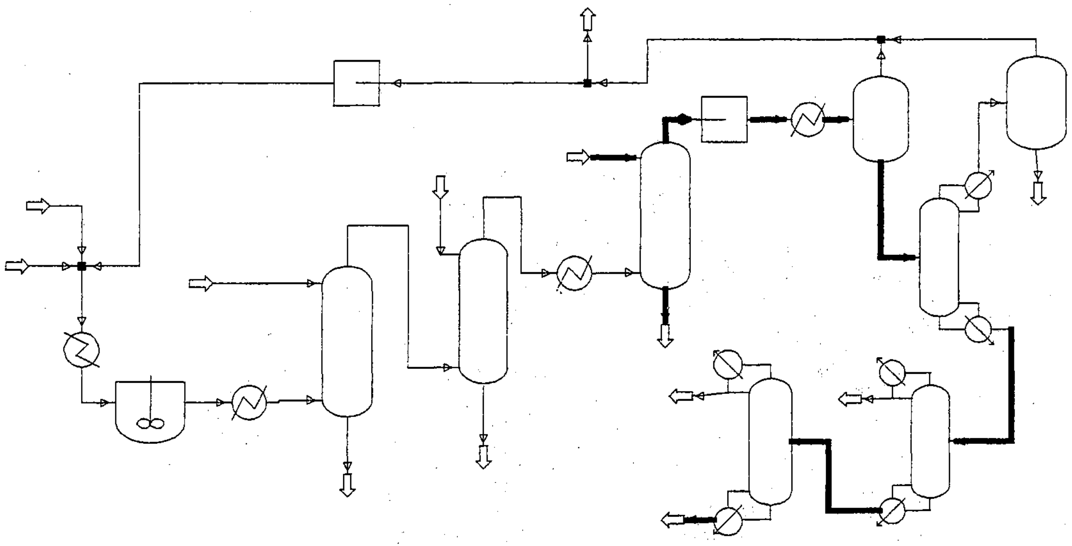

Figure G.9: Sulfuric acid SFC

APPENDIX H

OPTIMIZATION OF THE METHYL CHLORIDE PROCESS

```
TITLE 'Methyl Chloride Base Case Model'

IN-UNITS ENG

DEF-STREAMS CONVEN ALL

DIAGNOSTICS
    TERMINAL SIM-LEVEL=0 CONV-LEVEL=0 COST-LEVEL=0 PROP-LEVEL=0 &
        ECON-LEVEL=0 STREAM-LEVEL=0 SYS-LEVEL=0

RUN-CONTROL MAX-TIME=10000 MAX-FORT-ERR=1000

DATABANKS ASPENPCD  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        PURECOMP

PROP-SOURCES ASPENPCD  / AQUEOUS  / SOLIDS / INORGANIC  /  &
        PURECOMP

COMPONENTS
    H2O H2O H2O /
    CH4 CH4 CH4 /
    NAOH NAOH NAOH /
    NA+ NA+ NA+ /
    H3O+ H3O+ H3O+ /
    "NAOH(S)" NAOH "NAOH(S)" /
    OH- OH- OH- /
    CL2 CL2 CL2 /
    HCL HCL HCL /
    CH3CL CH3CL CH3CL /
    CH2CL2 CH2CL2 CH2CL2 /
    CHCL3 CHCL3 CHCL3 /
    CCL4 CCL4 CCL4 /
    HCLO HCLO HCLO /
    "NACL(S)" NACL "NACL(S)" /
    CLO- CLO- CLO- /
    CL- CL- CL- /
    H2SO4 H2SO4 H2SO4 /
    HSO4- HSO4- HSO4- /
    SO4-- SO4-2 SO4-- /
    N2 N2 N2

HENRY-COMPS ABS-DRY CL2 HCLO HCL CH4 CH3CL CH2CL2 CHCL3 CCL4

CHEMISTRY ABS
    STOIC 1 H2O -2 / H3O+ 1 / OH- 1
    STOIC 2 HCL -1 / H2O -1 / H3O+ 1 / CL- 1
    STOIC 3 CL2 -1 / H2O -2 / HCLO 1 / H3O+ 1 / CL- 1
    STOIC 4 HCLO -1 / H2O -1 / CLO- 1 / H3O+ 1
    K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0
    K-STOIC 3 A=-11.37532 B=-1286.972 C=0 D=0
    K-STOIC 4 A=-16.1519 B=-1602.87 C=0 D=0

CHEMISTRY DRY1
    DISS NAOH NA+ 1 / OH- 1
```

```
    STOIC 1 H2O -2 / H3O+ 1 / OH- 1
    STOIC 2 HCL -1 / H2O -1 / H3O+ 1 / CL- 1
    STOIC 3 CL2 -1 / H2O -2 / HCLO 1 / H3O+ 1 / CL- 1
    STOIC 4 HCLO -1 / H2O -1 / CLO- 1 / H3O+ 1
    K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0
    K-STOIC 3 A=-11.37532 B=-1286.972 C=0 D=0
    K-STOIC 4 A=-16.1519 B=-1602.87 C=0 D=0
    SALT "NACL(S)" NA+ 1 / CL- 1
    SALT "NAOH(S)" NA+ 1 / OH- 1
    K-SALT "NACL(S)" A=-203.5875 B=4381.176 C=35.87518  &
        D=-.06721607

CHEMISTRY DRY2
    STOIC 1 H2O -2 / H3O+ 1 / OH- 1
    STOIC 2 H2SO4 -1 / H2O -1 / H3O+ 1 / HSO4- 1
    STOIC 3 HSO4- -1 / H2O -1 / H3O+ 1 / SO4-- 1
    K-STOIC 1 A=132.89888 B=-13445.9 C=-22.4773 D=0

FLOWSHEET
    BLOCK DR1 IN=NAOH 5 OUT=6 W3
    BLOCK DR2 IN=H2SO4 7 OUT=8 W4
    BLOCK HX3 IN=6 OUT=7
    BLOCK ABS IN=H2O 4 OUT=5 W2
    BLOCK CMP1 IN=8 OUT=9
    BLOCK HX4 IN=9 OUT=10
    BLOCK FL1 IN=10 OUT=11 12
    BLOCK D1 IN=12 OUT=15 13
    BLOCK D2 IN=13 OUT=CH2CL2 14
    BLOCK D3 IN=14 OUT=CHCL3 W5
    BLOCK MX1 IN=19 48 OUT=1
    BLOCK CSTR IN=2A1 OUT=2A2
    BLOCK HX1 IN=1 OUT=2
    BLOCK CMP2 IN=18 OUT=19
    BLOCK SPL IN=17 OUT=WPRG 18
    BLOCK FL2 IN=15 OUT=16 CH3CL
    BLOCK MX2 IN=16 11 OUT=17
    BLOCK HX2 IN=3 OUT=4
    BLOCK PLUG IN=2B2 OUT=2B3
    BLOCK MX3 IN=2A3 2B4 OUT=3
    BLOCK HX5 IN=2B1 OUT=2B2
    BLOCK DUP1 IN=2 OUT=2A1 2B1
    BLOCK M1 IN=2A2 OUT=2A3
    BLOCK M2 IN=2B3 OUT=2B4
    BLOCK B1 IN=CH4 CL2 OUT=49
    BLOCK B2 IN=49 OUT=48
    BLOCK B3 IN=W5 OUT=47

PROPERTIES NRTL-RK
    PROPERTIES ELECNRTL

PROP-DATA HENRY-1
    IN-UNITS ENG PRESSURE='N/SQM' TEMPERATURE=K PDROP=PSI
    PROP-LIST HENRY
    BPVAL CL2 H2O 169.5452000 -9487.1960 -20.81234000 0.0  &
```

```
        273.0000000 400.0000000
    BPVAL HCL H2O 58.45296000 -7762.83200 0.0 0.0 273.000  &
        400.0000000
    BPVAL HCLO H2O -20.00000000 0.0 0.0 0.0 273.0000000  &
        400.0000000
    BPVAL CH2CL2 H2O 29.104 -3817.0 0.0 0.0 283.0 308.0
    BPVAL CHCL3 H2O 32.294 -4612 0.0 0.0 283.0 308.0
    BPVAL CCL4 H2O 33.741 -4411.0 0.0 0.0 283.0 308.0
    BPVAL CH4 H2O 195.2940000 -9111.670000 -25.03790000  &
        1.43434000E-4 275.0000000 353.0000000
    BPVAL CH3CL H2O 184.0280000 -9768.620000 -23.4240 0.0  &
        277.0000000 353.0000000

PROP-DATA NRTL-1
    IN-UNITS ENG
    PROP-LIST NRTL
    BPVAL H2O HCLO 11.25094000 0.0 .30000000 0.0 0.0 0.0  &
        32.00000407 211.9999993
    BPVAL HCLO H2O -7.175849000 0.0 .30000000 0.0 0.0 0.0  &
        32.00000407 211.9999993

PROP-DATA VLCLK-1
    IN-UNITS ENG
    PROP-LIST VLCLK
    BPVAL NA+ OH- -.2209618842 1.168080748
    BPVAL NA+ CL- .2425544521 .4050617606
    BPVAL H3O+ CL- .5534556818 .2140997348
    BPVAL NA+ SO4-- .1389686094 1.974549497
    BPVAL H3O+ HSO4- .8778750527 .3242692779

PROP-DATA GMELCC-1
    IN-UNITS ENG
    PROP-LIST GMELCC
    PPVAL H2O ( NA+ OH- ) 6.737997000
    PPVAL ( NA+ OH- ) H2O -3.771221000
    PPVAL H2O ( NA+ CL- ) 5.980196000
    PPVAL ( NA+ CL- ) H2O -3.789168000
    PPVAL H2O ( NA+ HSO4- ) 7.663000000
    PPVAL ( NA+ HSO4- ) H2O -3.944000000
    PPVAL H2O ( NA+ SO4-- ) 7.689221000
    PPVAL ( NA+ SO4-- ) H2O -4.284786000
    PPVAL H2O ( H3O+ OH- ) 8.045000000
    PPVAL ( H3O+ OH- ) H2O -4.072000000
    PPVAL H2O ( H3O+ CL- ) 4.110129000
    PPVAL ( H3O+ CL- ) H2O -3.344103000
    PPVAL H2O ( H3O+ HSO4- ) 6.362000000
    PPVAL ( H3O+ HSO4- ) H2O -3.749000000
    PPVAL H2O ( H3O+ SO4-- ) 8.000000000
    PPVAL ( H3O+ SO4-- ) H2O -4.000000000
    PPVAL CL2 ( NA+ OH- ) 15.00000000
    PPVAL ( NA+ OH- ) CL2 -8.000000000
    PPVAL CL2 ( NA+ CLO- ) 15.00000000
    PPVAL ( NA+ CLO- ) CL2 -8.000000000
    PPVAL CL2 ( NA+ CL- ) 15.00000000
```

```
    PPVAL ( NA+ CL- ) CL2 -8.000000000
    PPVAL CL2 ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) CL2 -8.000000000
    PPVAL CL2 ( H3O+ CLO- ) 15.00000000
    PPVAL ( H3O+ CLO- ) CL2 -8.000000000
    PPVAL CL2 ( H3O+ CL- ) 15.00000000
    PPVAL ( H3O+ CL- ) CL2 -8.000000000
    PPVAL HCL ( NA+ OH- ) 15.00000000
    PPVAL ( NA+ OH- ) HCL -8.000000000
    PPVAL HCL ( NA+ CLO- ) 15.00000000
    PPVAL ( NA+ CLO- ) HCL -8.000000000
    PPVAL HCL ( NA+ CL- ) 15.00000000
    PPVAL ( NA+ CL- ) HCL -8.000000000
    PPVAL HCL ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) HCL -8.000000000
    PPVAL HCL ( H3O+ CLO- ) 15.00000000
    PPVAL ( H3O+ CLO- ) HCL -8.000000000
    PPVAL HCL ( H3O+ CL- ) 12.00000000
    PPVAL ( H3O+ CL- ) HCL -1.0000000E-3
    PPVAL HCL ( H3O+ HSO4- ) 10.00000000
    PPVAL ( H3O+ HSO4- ) HCL -2.000000000
    PPVAL HCL ( H3O+ SO4-- ) 15.00000000
    PPVAL ( H3O+ SO4-- ) HCL -8.000000000
    PPVAL HCLO ( NA+ OH- ) 15.00000000
    PPVAL ( NA+ OH- ) HCLO -8.000000000
    PPVAL HCLO ( NA+ CLO- ) 15.00000000
    PPVAL ( NA+ CLO- ) HCLO -8.000000000
    PPVAL HCLO ( NA+ CL- ) 15.00000000
    PPVAL ( NA+ CL- ) HCLO -8.000000000
    PPVAL HCLO ( H3O+ OH- ) 15.00000000
    PPVAL ( H3O+ OH- ) HCLO -8.000000000
    PPVAL HCLO ( H3O+ CLO- ) 15.00000000
    PPVAL ( H3O+ CLO- ) HCLO -8.000000000
    PPVAL HCLO ( H3O+ CL- ) 15.00000000
    PPVAL ( H3O+ CL- ) HCLO -8.000000000
    PPVAL H2SO4 ( H3O+ CL- ) 10.00000000
    PPVAL ( H3O+ CL- ) H2SO4 -2.000000000
    PPVAL H2SO4 ( H3O+ HSO4- ) 12.99200000
    PPVAL ( H3O+ HSO4- ) H2SO4 -2.981000000
    PPVAL H2SO4 ( H3O+ SO4-- ) 8.000000000
    PPVAL ( H3O+ SO4-- ) H2SO4 -4.000000000
    PPVAL ( NA+ OH- ) ( NA+ CL- ) 8.407678000
    PPVAL ( NA+ CL- ) ( NA+ OH- ) 1.950440000
    PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 3.147792000
    PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -.5387706000
    PPVAL ( NA+ CL- ) ( NA+ SO4-- ) -11.44869000
    PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -.2697454000
    PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) .9536271000
    PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0

PROP-DATA GMELCD-1
    IN-UNITS ENG
    PROP-LIST GMELCD
    PPVAL H2O ( NA+ OH- ) 2556.435478
```

```
PPVAL ( NA+ OH- ) H2O -849.2763195
PPVAL H2O ( NA+ CL- ) 1514.732508
PPVAL ( NA+ CL- ) H2O -389.4562614
PPVAL H2O ( NA+ SO4-- ) 1018.076891
PPVAL ( NA+ SO4-- ) H2O -102.3078191
PPVAL H2O ( H3O+ CL- ) 4151.955402
PPVAL ( H3O+ CL- ) H2O -1176.370324
PPVAL H2O ( H3O+ HSO4- ) 3524.759832
PPVAL ( H3O+ HSO4- ) H2O -1049.759950
PPVAL H2O ( H3O+ SO4-- ) 0.0
PPVAL ( H3O+ SO4-- ) H2O 0.0
PPVAL CL2 ( NA+ OH- ) 0.0
PPVAL ( NA+ OH- ) CL2 0.0
PPVAL CL2 ( NA+ CLO- ) 0.0
PPVAL ( NA+ CLO- ) CL2 0.0
PPVAL CL2 ( NA+ CL- ) 0.0
PPVAL ( NA+ CL- ) CL2 0.0
PPVAL CL2 ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) CL2 0.0
PPVAL CL2 ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) CL2 0.0
PPVAL CL2 ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) CL2 0.0
PPVAL HCL ( NA+ OH- ) 0.0
PPVAL ( NA+ OH- ) HCL 0.0
PPVAL HCL ( NA+ CLO- ) 0.0
PPVAL ( NA+ CLO- ) HCL 0.0
PPVAL HCL ( NA+ CL- ) 0.0
PPVAL ( NA+ CL- ) HCL 0.0
PPVAL HCL ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) HCL 0.0
PPVAL HCL ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) HCL 0.0
PPVAL HCL ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) HCL 0.0
PPVAL HCL ( H3O+ HSO4- ) 0.0
PPVAL ( H3O+ HSO4- ) HCL 0.0
PPVAL HCL ( H3O+ SO4-- ) 0.0
PPVAL ( H3O+ SO4-- ) HCL 0.0
PPVAL HCLO ( NA+ OH- ) 0.0
PPVAL ( NA+ OH- ) HCLO 0.0
PPVAL HCLO ( NA+ CLO- ) 0.0
PPVAL ( NA+ CLO- ) HCLO 0.0
PPVAL HCLO ( NA+ CL- ) 0.0
PPVAL ( NA+ CL- ) HCLO 0.0
PPVAL HCLO ( H3O+ OH- ) 0.0
PPVAL ( H3O+ OH- ) HCLO 0.0
PPVAL HCLO ( H3O+ CLO- ) 0.0
PPVAL ( H3O+ CLO- ) HCLO 0.0
PPVAL HCLO ( H3O+ CL- ) 0.0
PPVAL ( H3O+ CL- ) HCLO 0.0
PPVAL H2SO4 ( H3O+ HSO4- ) -3119.219851
PPVAL ( H3O+ HSO4- ) H2SO4 -292.1399861
PPVAL H2SO4 ( H3O+ SO4-- ) 0.0
```

```
    PPVAL ( H3O+ SO4-- ) H2SO4 0.0
    PPVAL ( NA+ OH- ) ( NA+ CL- ) -324.8080045
    PPVAL ( NA+ CL- ) ( NA+ OH- ) -1491.716269
    PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 1408.793693
    PPVAL ( NA+ SO4-- ) ( NA+ OH- ) -170.8229619
    PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 6763.469077
    PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -240.5010485
    PPVAL ( H3O+ CL- ) ( H3O+ HSO4- ) -363.1438627
    PPVAL ( H3O+ HSO4- ) ( H3O+ CL- ) 0.0

PROP-DATA GMELCE-1
    IN-UNITS ENG
    PROP-LIST GMELCE
    PPVAL H2O ( NA+ OH- ) 3.013932000
    PPVAL ( NA+ OH- ) H2O 2.136557000
    PPVAL H2O ( NA+ CL- ) 7.433500000
    PPVAL ( NA+ CL- ) H2O -1.100418000
    PPVAL H2O ( NA+ SO4-- ) -14.08276000
    PPVAL ( NA+ SO4-- ) H2O 8.547499000
    PPVAL H2O ( H3O+ CL- ) .3417959000
    PPVAL ( H3O+ CL- ) H2O 2.121453000
    PPVAL H2O ( H3O+ HSO4- ) -4.599000000
    PPVAL ( H3O+ HSO4- ) H2O 4.472000000
    PPVAL CL2 ( NA+ OH- ) 0.0
    PPVAL ( NA+ OH- ) CL2 0.0
    PPVAL CL2 ( NA+ CLO- ) 0.0
    PPVAL ( NA+ CLO- ) CL2 0.0
    PPVAL CL2 ( NA+ CL- ) 0.0
    PPVAL ( NA+ CL- ) CL2 0.0
    PPVAL CL2 ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) CL2 0.0
    PPVAL CL2 ( H3O+ CLO- ) 0.0
    PPVAL ( H3O+ CLO- ) CL2 0.0
    PPVAL CL2 ( H3O+ CL- ) 0.0
    PPVAL ( H3O+ CL- ) CL2 0.0
    PPVAL HCL ( NA+ OH- ) 0.0
    PPVAL ( NA+ OH- ) HCL 0.0
    PPVAL HCL ( NA+ CLO- ) 0.0
    PPVAL ( NA+ CLO- ) HCL 0.0
    PPVAL HCL ( NA+ CL- ) 0.0
    PPVAL ( NA+ CL- ) HCL 0.0
    PPVAL HCL ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) HCL 0.0
    PPVAL HCL ( H3O+ CLO- ) 0.0
    PPVAL ( H3O+ CLO- ) HCL 0.0
    PPVAL HCL ( H3O+ CL- ) 0.0
    PPVAL ( H3O+ CL- ) HCL 0.0
    PPVAL HCL ( H3O+ SO4-- ) 0.0
    PPVAL ( H3O+ SO4-- ) HCL 0.0
    PPVAL HCLO ( NA+ OH- ) 0.0
    PPVAL ( NA+ OH- ) HCLO 0.0
    PPVAL HCLO ( NA+ CLO- ) 0.0
    PPVAL ( NA+ CLO- ) HCLO 0.0
    PPVAL HCLO ( NA+ CL- ) 0.0
```

```
    PPVAL ( NA+ CL- ) HCLO 0.0
    PPVAL HCLO ( H3O+ OH- ) 0.0
    PPVAL ( H3O+ OH- ) HCLO 0.0
    PPVAL HCLO ( H3O+ CLO- ) 0.0
    PPVAL ( H3O+ CLO- ) HCLO 0.0
    PPVAL HCLO ( H3O+ CL- ) 0.0
    PPVAL ( H3O+ CL- ) HCLO 0.0
    PPVAL H2SO4 ( H3O+ HSO4- ) -30.12600000
    PPVAL ( H3O+ HSO4- ) H2SO4 .8060000000
    PPVAL ( NA+ OH- ) ( NA+ CL- ) 100.0000000
    PPVAL ( NA+ CL- ) ( NA+ OH- ) 6.619543000
    PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 43.39265000
    PPVAL ( NA+ SO4-- ) ( NA+ OH- ) 4.518955000
    PPVAL ( NA+ CL- ) ( NA+ SO4-- ) 60.25378000
    PPVAL ( NA+ SO4-- ) ( NA+ CL- ) -4.302999000

PROP-DATA GMELCN-1
    IN-UNITS ENG
    PROP-LIST GMELCN
    PPVAL H2O ( NA+ OH- ) .2000000000
    PPVAL H2O ( NA+ CL- ) .2000000000
    PPVAL H2O ( NA+ SO4-- ) .2000000000
    PPVAL H2O ( H3O+ HSO4- ) .2000000000
    PPVAL CL2 ( NA+ OH- ) .1000000000
    PPVAL CL2 ( NA+ CLO- ) .1000000000
    PPVAL CL2 ( NA+ CL- ) .1000000000
    PPVAL CL2 ( H3O+ OH- ) .1000000000
    PPVAL CL2 ( H3O+ CLO- ) .1000000000
    PPVAL CL2 ( H3O+ CL- ) .1000000000
    PPVAL HCL ( NA+ OH- ) .1000000000
    PPVAL HCL ( NA+ CLO- ) .1000000000
    PPVAL HCL ( NA+ CL- ) .1000000000
    PPVAL HCL ( H3O+ OH- ) .1000000000
    PPVAL HCL ( H3O+ CLO- ) .1000000000
    PPVAL HCL ( H3O+ SO4-- ) .1000000000
    PPVAL HCLO ( NA+ OH- ) .1000000000
    PPVAL HCLO ( NA+ CLO- ) .1000000000
    PPVAL HCLO ( NA+ CL- ) .1000000000
    PPVAL HCLO ( H3O+ OH- ) .1000000000
    PPVAL HCLO ( H3O+ CLO- ) .1000000000
    PPVAL HCLO ( H3O+ CL- ) .1000000000
    PPVAL H2SO4 ( H3O+ HSO4- ) .2000000000

STREAM CH4
    SUBSTREAM MIXED TEMP=77 PRES=14.7 MOLE-FLOW=323
    MOLE-FRAC CH4 0.98 / N2 0.02

STREAM CL2
    SUBSTREAM MIXED TEMP=77 PRES=14.7
    MOLE-FLOW CL2 320

STREAM H2O
    SUBSTREAM MIXED TEMP=90 PRES=14.7
    MOLE-FLOW H2O 2025
```

```
STREAM H2SO4
    SUBSTREAM MIXED TEMP=77 PRES=14.7 MOLE-FLOW=200
    MOLE-FRAC H2SO4 1

STREAM NAOH
    SUBSTREAM MIXED TEMP=86 PRES=14.7 NPHASE=1 PHASE=S
    MOLE-FLOW NAOH 200

BLOCK MX1 MIXER

BLOCK MX2 MIXER

BLOCK MX3 MIXER

BLOCK SPL FSPLIT
    FRAC WPRG 0.1

BLOCK B1 HEATER
    PARAM TEMP=77 PRES=0

BLOCK B2 HEATER
    PARAM TEMP=77 PRES=0

BLOCK B3 HEATER
    PARAM TEMP=77 PRES=0

BLOCK HX1 HEATER
    PARAM TEMP=572 PRES=0

BLOCK HX2 HEATER
    PARAM TEMP=100 PRES=0

BLOCK HX3 HEATER
    PARAM TEMP=100 PRES=0

BLOCK HX4 HEATER
    PARAM TEMP=-58 PRES=0

BLOCK HX5 HEATER
    PARAM TEMP=977 PRES=0

BLOCK FL1 FLASH2
    PARAM PRES=0 DUTY=0

BLOCK FL2 FLASH2
    PARAM TEMP=-100 PRES=0

BLOCK D3 DSTWU
    PARAM LIGHTKEY=CHCL3 RECOVL=0.999 HEAVYKEY=CCL4   &
        RECOVH=0.001 PTOP=14.7 PBOT=14.7 NSTAGE=10
    SIZE-DATA COND=YES REB=YES
```

```
BLOCK ABS RADFRAC
    PARAM NSTAGE=2
    FEEDS H2O 1 ON-STAGE / 4 2 ON-STAGE
    PRODUCTS 5 1 V / W2 2 L
    P-SPEC 1 14.7
    COL-SPECS Q1=0 QN=0 MOLE-RDV=1
    PROPERTIES ELECNRTL HENRY-COMPS=ABS-DRY CHEMISTRY=ABS  &
        TRUE-COMPS=NO

BLOCK D1 RADFRAC
    PARAM NSTAGE=12
    FEEDS 12 6
    PRODUCTS 13 12 L / 15 1 V
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RDV=1 MOLE-RR=1.2
    SPEC 1 MOLE-RECOV 0.995 COMPS=CH3CL STREAMS=15
    VARY 1 D:F 0.001 0.999
    SIZE-DATA COND=YES REB=YES

BLOCK D2 RADFRAC
    PARAM NSTAGE=20
    FEEDS 13 10
    PRODUCTS CH2CL2 1 L / 14 20 L
    P-SPEC 1 14.7
    COL-SPECS D:F=0.5 MOLE-RDV=0 MOLE-RR=1.5
    SPEC 1 MOLE-RECOV 0.999 COMPS=CH2CL2 STREAMS=CH2CL2
    VARY 1 D:F 0.001 0.999
    SIZE-DATA COND=YES REB=YES

BLOCK DR1 SEP
>
    FRAC STREAM=W3 SUBSTREAM=MIXED COMPS=H2O CH4 NAOH NA+  &
>
        H3O+ "NAOH(S)" OH- CL2 HCL CH3CL CH2CL2 CHCL3 CCL4  &
>
        HCLO "NACL(S)" CLO- CL- H2SO4 HSO4- SO4-- N2 FRACS= &
>
        0.3 0 1 1 1 1 1 0 1 0 0 0 0 0 1 1 1 0 0 0  &
        0

BLOCK DR2 RADFRAC
    PARAM NSTAGE=2
    FEEDS H2SO4 1 ON-STAGE / 7 2 ON-STAGE
    PRODUCTS 8 1 V / W4 2 L
    P-SPEC 1 14.7
    COL-SPECS Q1=0 QN=0 MOLE-RDV=1
    PROPERTIES ELECNRTL HENRY-COMPS=ABS-DRY CHEMISTRY=DRY2 &
        TRUE-COMPS=NO
    BLOCK-OPTION RESTART=NO

BLOCK CSTR RCSTR
    PARAM VOL=1600 TEMP=525 <C> PRES=0
    REACTIONS RXN-IDS=RSCH-1
```

```
BLOCK PLUG RPLUG
    PARAM TYPE=T-SPEC LENGTH=60 DIAM=3
    REACTIONS RXN-IDS=RSCH-1

BLOCK CMP1 COMPR
    PARAM TYPE=ASME-POLYTROP PRES=115 TEMP=275

BLOCK CMP2 COMPR
    PARAM TYPE=ASME-POLYTROP DELP=45 NPHASE=2

BLOCK M1 MULT
    PARAM FACTOR=0

BLOCK M2 MULT
    PARAM FACTOR=1

BLOCK DUP1 DUPL

CBLOCK E-3 COMPR
    UTILITY ELEC=U-ELEC
    REFERENCE BLOCK=CMP1

CBLOCK E-11 COMPR
    UTILITY ELEC=U-ELEC
    REFERENCE BLOCK=CMP2

CBLOCK E-1 HEATX
    SIZING-DATA NPASS-SHELL=2 NPASS-TUBE=4
    REFERENCE TUBE UTILITY=U-WAT
    REFERENCE SHELL BLOCK=HX2

CBLOCK E-2 HEATX
    SIZING-DATA NPASS-SHELL=2 NPASS-TUBE=4
    REFERENCE TUBE UTILITY=U-WAT
    REFERENCE SHELL BLOCK=HX3

CBLOCK E-4 HEATX
    REFERENCE TUBE UTILITY=U-WATCH
    REFERENCE SHELL BLOCK=D2 STAGE=TOP

CBLOCK E-5 HEATX
    REFERENCE TUBE UTILITY=U-WAT
    REFERENCE SHELL BLOCK=D3 STAGE=TOP

CBLOCK E-6 HEATX
    REFERENCE TUBE UTILITY=U-STEH
    REFERENCE SHELL BLOCK=HX1

CBLOCK E-7 HEATX
    REFERENCE TUBE UTILITY=U-STEL
    REFERENCE SHELL BLOCK=D1 STAGE=BOTTOM

CBLOCK E-8 HEATX
    REFERENCE TUBE UTILITY=U-STEL
```

```
    REFERENCE SHELL BLOCK=D2 STAGE=BOTTOM

CBLOCK E-9 HEATX
    REFERENCE TUBE UTILITY=U-STEL
    REFERENCE SHELL BLOCK=D3 STAGE=BOTTOM

CBLOCK E-10 H-VESSEL
    SIZING-DATA VOL=500
    REFERENCE BLOCK=PLUG

UTILITY U-WAT WATER
    PROPERTIES STEAM-TA
    COST PRICE=6.868E-6 <$/KG>
    PARAM COMPONENT=H2O TIN=90 TOUT=120

UTILITY U-WATCH WATER
    PROPERTIES STEAM-TA
    COST PRICE=1.374E-5
    PARAM COMPONENT=H2O TOUT=90

UTILITY U-ELEC ELECTRICITY
    COST PRICE=0.035

UTILITY U-STEH STEAM
    PROPERTIES STEAM-TA
    COST PRICE=0.00455
    PARAM COMPONENT=H2O PRES=600 <PSIG> TIN=750 TOUT=750

UTILITY U-STEL STEAM
    PROPERTIES STEAM-TA
    COST PRICE=0.00245
    PARAM COMPONENT=H2O PRES=50 <PSIG>

DESIGN-SPEC DS-1
    DEFINE H2O MOLE-FRAC STREAM=8 SUBSTREAM=MIXED COMPONENT=H2O
    SPEC "H2O" TO "0.00003"
    TOL-SPEC "0.00002"
    VARY MOLE-FLOW STREAM=H2SO4 SUBSTREAM=MIXED COMPONENT=H2SO4
    LIMITS "200" "500"

FORTRAN AEP
F     COMMON /FUNC/ AEP,ENVI
F     DIMENSION PR(21)
F     REAL IRR, LC, IF, NPV
    VECTOR-DEF CL2 STREAM CL2
    VECTOR-DEF CH4 STREAM CH4
    VECTOR-DEF H2SO4 STREAM H2SO4
    VECTOR-DEF H2O STREAM H2O
    DEFINE ELEC UTILITY-VAR UTILITY= U-ELEC VARIABLE=COST  &
        SENTENCE=RESULTS
    DEFINE WAT UTILITY-VAR UTILITY= U-WAT VARIABLE=COST  &
        SENTENCE=RESULTS
    DEFINE WATCH UTILITY-VAR UTILITY=U-WATCH VARIABLE=COST &
        SENTENCE=RESULTS
```

```
    DEFINE STEL UTILITY-VAR UTILITY= U-STEL VARIABLE=COST  &
        SENTENCE=RESULTS
    DEFINE STEH UTILITY-VAR UTILITY= U-STEH VARIABLE=COST  &
        SENTENCE=RESULTS
    VECTOR-DEF CH3CL STREAM CH3CL
    VECTOR-DEF CH2CL2 STREAM CH2CL2
    VECTOR-DEF CHCL3 STREAM CHCL3
    VECTOR-DEF W2 STREAM W2
    VECTOR-DEF W3 STREAM W3
    VECTOR-DEF W4 STREAM W5
    VECTOR-DEF WPRG STREAM WPRG
    VECTOR-DEF SOD STREAM NAOH
    VECTOR-DEF W5 STREAM W5
    DEFINE D1 BLOCK-VAR BLOCK=D1 VARIABLE=COND-DUTY  &
        SENTENCE=RESULTS
    DEFINE HX4 BLOCK-VAR BLOCK=HX4 VARIABLE=QCALC  &
        SENTENCE=PARAM
    DEFINE WCS UTILITY-VAR UTILITY= U-WAT VARIABLE=PRICE  &
        SENTENCE=COST
    DEFINE CPLUG CBLOCK-VAR CBLOCK=E-10 VARIABLE=TOT-COST  &
        SENTENCE=RESULTS
    DEFINE FM2 BLOCK-VAR BLOCK=M2 VARIABLE=FACTOR  &
        SENTENCE=PARAM
    DEFINE FL2 BLOCK-VAR BLOCK=FL2 VARIABLE=QCALC  &
        SENTENCE=PARAM
C   ** VARIABLE DEFINITION **
F      HR=8150.0
F      HC=3600.0
C  ****PRICES*****
C  1:H2O    2:CH4     3:NAOH   8:CL2   9:HCL
C 10:CH3CL 11:CH2CL2 12:CHCL3 13:CCL4 18:H2SO4
C  ***************
F      DO 10 I=1,21
F         PR(I)=0
F 10   CONTINUE
F      PR(1)=0.000055
F      PR(2)=1.25
F      PR(3)=150.0
F      PR(8)=19.88
F      PR(9)=5.11
F      PR(10)=19.19
F      PR(11)=80.75
F      PR(12)=78.9
F      PR(13)=0
F      PR(18)=3.72
C   ** ECONOMIC MODEL **
C      *RAW MATERIALS ($/YR)*
F      RAW=(CL2(22)*PR(8)+CH4(22)*PR(2))*HC*HR
C      *SOLVENTS ($/YR)*
F      SOL1=SOD(3)*PR(3)*0.02
F      SOL2=H2O(22)*PR(1)
F      SOL3=H2SO4(22)*0.02*PR(8)
F      SOL=(SOL1+SOL2+SOL3)*HC*HR
C      *UTILITIES ($/YR)*
```

```
F       RFD=D1+HX4+FL2
F       PWRF=(-9.18E-6)*RFD
F       WCV=-30.0
F       CD=3.06*(RFD)*WCS/WCV
F       REF=(CD+PWRF)*HR
F       UT=ELEC+WAT+WATCH+STEL+STEH
F       UTIL=(UT*HR/8772)+REF
C       *REVENUE ($/YR)*
F       PROD=CH3CL(10)*PR(10)
F       CPROD=CH2CL2(22)*PR(11)+CHCL3(22)*PR(12)
F       BPROD=W2(9)*PR(9)*0.95/0.31
F       REV=(PROD+CPROD+BPRD)*HC*HR
C       WRITE(NTERM,*) 'RAW,SOL,UTIL',RAW,SOL,UTIL
F       PROFIT=REV-RAW-SOL-UTIL
C       WRITE(NTERM,*) 'REV,PROFIT',REV,PROFIT
C       *DIRECT COSTS*
F       PW2=0
F       PW3=0
F       PW4=0
F       PW5=0
F       PWP=0
F       DO 20 I=1,21
F          PW2=PW2+W2(I)*PR(I)*0.05
F          PW3=PW3+W3(I)*PR(I)*0.02
F          PW4=PW4+W4(I)*PR(I)*0.02
F          PW5=PW5+W5(I)*PR(I)
F          PWP=PWP+WPRG(I)*PR(I)
F 20    CONTINUE
F       PW=(PW2+PW3+PW4+PW5+PWP)*HR*HC
C      *WASTE TREATMENT ($/YR)*
F       TPG=110*2118.6*WPRG(22)*WPRG(30)/WPRG(29)
F       WLB=W2(22)*W2(30)*2.2*HC*HR
F       TW2A=(5.5E-6)*WLB**.7+.912*WLB**0.5
F       TW2=TW2A+(4.36E-6)*WLB
F       WT=TPG+TW2
C       WRITE(NTERM,*) 'PW,WT',PW,WT
C      *HIDDEN COSTS ($/YR)*
F       HIDC=100000
C      *LIABILITY COSTS*
F       LC=(7.55*.1+67*.1+50*.1+3*.1*0.78*.1)*1000
C      *DISPOSAL COSTS*
F       DCW2=W2(22)*W2(30)/W2(29)
F       DCW3=W3(22)*W3(30)/W3(29)
F       DCW4=W4(22)*W4(30)/W4(29)
F       DC=(DCW2*0.05+DCW3*0.02+DCW4*0.02)*HR*HC
C       WRITE(NTERM,*) 'HI,LC,DC',HIDC,LC,DC
F       APR=PROFIT-PW-WT-HIDC-LC-DC
C       WRITE(NTERM,*) 'APR',APR
C    ** CAPITAL COST **
F       CC=0.0
F       CC=CPLUG*FM2
F       WRITE(NTERM,*) 'CC',CC
C    ** ANNUAL EQUIVALENT PROFIT **
F       IRR=0.1
```

```
F       NY=5
F       TX=0.34
F       IF=0.025
F       ANF=(IRR*(1+IRR)**NY)/((1+IRR)**NY-1)
F       NPV=0
F       IF (CC .GT. 0) NPV=-CC
C       WRITE(NTERM,*) 'NPV',NPV
F       DO 30 I=1,NY
F          FI=(1+IF)**I
F          FD=CC/NY
F          NPV=NPV+(APR*FI*(1-TX)+FD*TX)/(1+IRR)**I
F 30    CONTINUE
F       AEP=NPV*ANF
F       WRITE(NTERM,*) 'NPV,AEP',NPV,AEP
    EXECUTE LAST

;The variable U1 represents the non-waste stream release ;factor
;The variable U2 represents the environmental impact index ;of
methyl chloride

FORTRAN CONTROL
F      COMMON /RAND/ IX, IY, IIZ
F      COMMON /CONT/ LOOP, LOOP2, ICK, IN, IN2, ACC, ICK2
F      COMMON /ANNEAL/ T, TLEV, ALFA, EMOBJ, ML, QOBJ, QCNT
F      COMMON /STAT/ OBJ(1000), RES(500), RESN(500)
F      COMMON /SSIZE/ SAMP, NSAMP, NSA
F      REAL L,H,M,MO
    DEFINE U1 PARAMETER 1
    DEFINE U2 PARAMETER 2
    DEFINE U3 UTILITY-VAR UTILITY= U-STEH VARIABLE=PRICE  &
        SENTENCE=COST
    DEFINE X1 BLOCK-VAR BLOCK=CSTR VARIABLE=TEMP   &
        SENTENCE=PARAM
    DEFINE X1OLD PARAMETER 3
    DEFINE X2 STREAM-VAR STREAM=CL2 SUBSTREAM=MIXED  &
        VARIABLE=MOLE-FLOW
    DEFINE X2OLD PARAMETER 4
    DEFINE X3 BLOCK-VAR BLOCK=HX5 VARIABLE=TEMP    &
         SENTENCE=PARAM
    DEFINE X3OLD PARAMETER 5
    DEFINE Y1 BLOCK-VAR BLOCK=M1 VARIABLE=FACTOR  &
        SENTENCE=PARAM
    DEFINE Y1OLD PARAMETER 6
    DEFINE Y1B BLOCK-VAR BLOCK=M2 VARIABLE=FACTOR  &
        SENTENCE=PARAM
    DEFINE T3 BLOCK-VAR BLOCK=B3 VARIABLE=TEMP  &
        SENTENCE=PARAM
F      WRITE(NTERM,*) 'T,ALFA,TLEVEL',T,ALFA,TLEV
F      WRITE(NTERM,*) 'ML,ACC',ML,ACC
F      IF (ICK .EQ. 1) THEN
F         LOOP2=LOOP2+1
C      ** CHECK WHETER EQUILIBRIUM HAS BEEN REACHED **
F         IF ((LOOP2 .GT. ML) .OR. (ACC .GT. 10)) GOTO 40
F         T3=T3+0.1*LOOP2
```

```
F          WRITE(NTERM,*) 'T3',T3
C       ** DETERMINATION OF RANDOM NUMBER OF SAMPLES **
F 25         R=RDM()
F            IF (R .LE. 0.5) S=SAMP-5*RDM()
F            IF (R .GT. 0.5) S=SAMP+5*RDM()
F            IF (S .LT. 2) GOTO 25
F            SAMP=S
F            NSAMP=IDINT(SAMP)
F            WRITE(NTERM,*) 'NSAMP',NSAMP
C       ** NEW VALUES FOR OPTIMIZATION VARIABLES **
F            X1OLD=X1
F 15         X1=X1+(2*RDM()-1)*34
F            IF ((X1 .LT. 665) .OR. (X1 .GT. 1000)) GOTO 15
F            X2OLD=X2
F 16         X2=X2+(2*RDM()-1)*7
F            IF ((X2 .LT. 285) .OR. (X2 .GT. 355)) GOTO 16
F            X3OLD=X3
F 17         X3=X3+(2*RDM()-1)*34
F            IF ((X3 .LT. 665) .OR. (X3 .GT. 1000)) GOTO 17
F            Y1OLD=Y1
F            IF (RDM() .GT. 0.5) THEN
F               Y1=1
F               Y1B=0
F            ELSE
F               Y1=0
F               Y1B=1
F            END IF
F            WRITE(NTERM,*) 'LP2 DF:X1,X2,X3,Y1'
F            WRITE(NTERM,*) LOOP2,X1,X2,X3,Y1
F            ICK=0
F            LOOP=0
F            IF (IN .EQ. 0) T3=77
F       END IF
C       ** SAMPLING OF UNCERTAIN PARAMETERS **
C          ** RELEASE FACTOR **
F       L=0.05
F       H=0.3
F       MO=0.1
F       M=(MO-L)/(H-L)
F       U=RDM()
F       IF (U .LE. M) THEN
F          U1=L+((U*(H-L)*MO-L))**0.5
F       ELSE
F          U1=H-((1-U)*(H-L)*(H-MO))**0.5
F       END IF
C          ** ENVIRONMENTAL IMPACT **
F       U2=RDM()*(34.7-16.1)+16.1
C          ** STEAM COST **
F 20    V1=2*RDM()-1
F       V2=2*RDM()-1
F       VW=V1*V1+V2*V2
F       IF (VW .GT. 1) GOTO 20
F       YY=(-2*DLOG(VW)/VW)**0.5
F       U3=0.00455+0.0001*V2*YY
```

```
F      WRITE(NTERM,*) 'U1,U2,U3',U1,U2,U3
F      GOTO 50
F 40   T=T*ALFA
F      RES(TLEV)=EMOBJ
F      RESN(TLEV)=NSA
F      TLEV=TLEV+1
F      ACC=0
F      RRR=ABS(EMOBJ-QOBJ)
F      IF (RRR .LT. TOL) THEN
F         QCNT=QCNT+1
F         WRITE(NTERM,*) 'QCNT',QCNT
F      ELSE
F         QCNT=0
F         QOBJ=EMOBJ
F      END IF
F      IF (QCNT .LE. 5) THEN
F         LOOP2=0
F         T3=77.0
F      END IF
F      IF (QCNT .GT. 5) THEN
F         DO 45 I=1,TLEV-1
F            WRITE(NTERM,*) I,RES(I),RESN(I)
F 45      CONTINUE
F         LOOP2=0
F      END IF
F      WRITE(NTERM,*) 'EQUIL REACHED',T,TLEV
F 50   IN=0
    EXECUTE AFTER BLOCK B2

FORTRAN EI
F       COMMON /FUNC/ AEP, ENVI
F       DIMENSION EI(21)
    VECTOR-DEF S1 STREAM 1
    VECTOR-DEF S2 STREAM 2
    VECTOR-DEF S3 STREAM 3
    VECTOR-DEF S4 STREAM 4
    VECTOR-DEF S5 STREAM 5
    VECTOR-DEF S6 STREAM 6
    VECTOR-DEF S7 STREAM 7
    VECTOR-DEF S8 STREAM 8
    VECTOR-DEF S9 STREAM 9
    VECTOR-DEF S10 STREAM 10
    VECTOR-DEF S11 STREAM 11
    VECTOR-DEF S12 STREAM 12
    VECTOR-DEF S13 STREAM 13
    VECTOR-DEF S14 STREAM 14
    VECTOR-DEF S15 STREAM 15
    VECTOR-DEF S16 STREAM 16
    VECTOR-DEF S17 STREAM 17
    VECTOR-DEF S18 STREAM 18
    VECTOR-DEF S19 STREAM 19
    VECTOR-DEF W2 STREAM W2
    VECTOR-DEF W3 STREAM W3
    VECTOR-DEF W4 STREAM W4
```

```
    VECTOR-DEF W5 STREAM W5
    VECTOR-DEF WPRG STREAM WPRG
    VECTOR-DEF CL2 STREAM CL2
    VECTOR-DEF CH4 STREAM CH4
    VECTOR-DEF H2SO4 STREAM H2SO4
    VECTOR-DEF CH3CL STREAM CH3CL
    VECTOR-DEF CH2CL2 STREAM CH2CL2
    VECTOR-DEF CHCL3 STREAM CHCL3
    DEFINE U1 PARAMETER 1
    DEFINE U2 PARAMETER 2
C ** ENVIRONMENTAL IMPACT INDEXES **
C  1:H2O    2:CH4     3:NAOH    8:CL2   9:HCL
C 10:CH3CL 11:CH2CL2 12:CHCL3 13:CCL4 18:H2SO4
F      DO 10 I=1,21
F         EI(I)=0.0
F 10   CONTINUE
F      EI(8)=89.5
F      EI(9)=80.2
F      EI(10)=34.7
F      EI(11)=51.8
F      EI(12)=67.8
F      EI(13)=72.2
F      EI(18)=100.4
F      RFS=U1
F      RFW=1.0
F      EI(10)=U2
F      S1I=0
F      S2I=0
F      S3I=0
F      S4I=0
F      S5I=0
F      S6I=0
F      S7I=0
F      S8I=0
F      S9I=0
F      S10I=0
F      S11I=0
F      S12I=0
F      S13I=0
F      S14I=0
F      S15I=0
F      S16I=0
F      S17I=0
F      S18I=0
F      S19I=0
F      W2I=0
F      W3I=0
F      W4I=0
F      W5I=0
F      WPI=0
F      CH3I=0
F      CH2I=0
F      CHI=0
F      ACSI=0
```

```
F     CH4I=0
F     CLI=0
F     DO 20 I=1,21
F        S1I=S1I+S1(I)*EI(I)*RFS
F        S2I=S2I+S2(I)*EI(I)*RFS
F        S3I=S3I+S3(I)*EI(I)*RFS
F        S4I=S4I+S4(I)*EI(I)*RFS
F        S5I=S5I+S5(I)*EI(I)*RFS
F        S6I=S6I+S6(I)*EI(I)*RFS
F        S7I=S7I+S7(I)*EI(I)*RFS
F        S8I=S8I+S8(I)*EI(I)*RFS
F        S9I=S9I+S9(I)*EI(I)*RFS
F        S10I=S10I+S10(I)*EI(I)*RFS
F        S11I=S11I+S11(I)*EI(I)*RFS
F        S12I=S12I+S12(I)*EI(I)*RFS
F        S13I=S13I+S13(I)*EI(I)*RFS
F        S14I=S14I+S14(I)*EI(I)*RFS
F        S15I=S15I+S15(I)*EI(I)*RFS
F        S16I=S16I+S16(I)*EI(I)*RFS
F        S17I=S17I+S17(I)*EI(I)*RFS
F        S18I=S18I+S18(I)*EI(I)*RFS
F        S19I=S19I+S19(I)*EI(I)*RFS
F        W2I=W2I+W2(I)*EI(I)*RFW
F        W3I=W3I+W3(I)*EI(I)*RFW
F        W4I=W4I+W4(I)*EI(I)*RFW
F        W5I=W5I+W5(I)*EI(I)*RFW
F        WPI=WPI+WPRG(I)*EI(I)*RFW
F        CH3I=CH3I+CH3CL(I)*EI(I)*RFS
F        CH2I=CH2I+CH2CL2(I)*EI(I)*RFS
F        CHI=CHI+CHCL3(I)*EI(I)*RFS
F        ACSI=ACSI+H2SO4(I)*EI(I)*RFS
F        CH4I=CH4I+CH4(I)*EI(I)*RFS
F        CLI=CLI+CL2(I)*EI(I)*RFS
F  20 CONTINUE
F     ENV1=S1I+S2I+S3I+S4I+S5I+S6I+S71+S8I
F     ENV2=S9I+S10I+S11I+S12I+S13I+S14I+S15I
F     ENV3=S16I+S17I+S18I+S19I+W2I+W3I+W4I+W5I
F     ENV4=WPI+CH3I+CH2I+CHI+ACSI+CH4I+CLI
F     ENVI=(ENV1+ENV2+ENV3+ENV4)/CH3CL(22)
F     WRITE(NTERM,*) 'ENV IMP',ENVI
    EXECUTE BEFORE FORTRAN AEP

FORTRAN INIT
F     COMMON /RAND/ IX, IY, IIZ
F     COMMON /CONT/ LOOP, LOOP2, ICK, IN, IN2, ACC, ICK2
F     COMMON /ANNEAL/ T, TLEV, ALFA, EMOBJ, ML, QOBJ, QCNT
F     COMMON /STAT/ OBJ(1000), RES(500), RESN(500)
F     COMMON /SSIZE/ SAMP, NSAMP, NSA
F     COMMON /STOP/ TOL
    DEFINE T3 BLOCK-VAR BLOCK=B3 VARIABLE=TEMP  &
        SENTENCE=PARAM
C  ** READ RANDOM SEED NUMBERS REQUIRED FOR SUBROUTINE **
F     WRITE (NTERM,*) 'RANDOM SEED NUMBER (IX) ?'
F     READ (NTERM,*) IX
```

```
F      WRITE (NTERM,*) 'RANDOM SEED NUMBER (IY) ?'
F      READ (NTERM,*) IY
F      WRITE (NTERM,*) 'RANDOM SEED NUMBER (IZ) ?'
F      READ (NTERM,*) IIZ
C   ** INITIALIZE CONTROL VARIABLES **
F      LOOP2=0
F      ICK=1
F      TLEV=1.0
F      IN=1
F      IN2=1
F      ICK2=1
F      QCNT=0
F      ACC=0
C   ** INITIALIZE USER SPECIFIED VARIABLES **
F      TOL=0.1
F      SAMP=5
F      T=75
F      ALFA=0.9
F      ML=30
    EXECUTE FIRST

FORTRAN STOC
F      COMMON /RAND/ IX, IY, IIZ
F      COMMON /CONT/ LOOP, LOOP2, ICK, IN, IN2, ACC, ICK2
F      COMMON /ANNEAL/ T, TLEV, ALFA, EMOBJ, ML, QOBJ, QCNT
F      COMMON /STAT/ OBJ(1000), RES(500), RESN(500)
F      COMMON /SSIZE/ SAMP, NSAMP, NSA
F      COMMON /FUNC/ AEP, ENVI
F      COMMON /STOP/ TOL
    DEFINE U1 PARAMETER 1
    DEFINE U2 PARAMETER 2
    DEFINE U3 UTILITY-VAR UTILITY= U-STEH VARIABLE=PRICE  &
        SENTENCE=COST
    DEFINE X1 BLOCK-VAR BLOCK=CSTR VARIABLE=TEMP &
         SENTENCE=PARAM
    DEFINE X1OLD PARAMETER 3
    DEFINE X2 STREAM-VAR STREAM=CL2 SUBSTREAM=MIXED  &
        VARIABLE=MOLE-FLOW
    DEFINE X2OLD PARAMETER 4
    DEFINE X3 BLOCK-VAR BLOCK=HX5 VARIABLE=TEMP &
         SENTENCE=PARAM
    DEFINE X3OLD PARAMETER 5
    DEFINE Y1 BLOCK-VAR BLOCK=M1 VARIABLE=FACTOR  &
         SENTENCE=PARAM
    DEFINE Y1OLD PARAMETER 6
    DEFINE T3 BLOCK-VAR BLOCK=B3 VARIABLE=TEMP  &
         SENTENCE=PARAM
F      IF (ICK2 .EQ. 1) GOTO 50
F      IF (LOOP2 .EQ. 0) GOTO 50
F      LOOP=LOOP+1
F      IF (LOOP .LT. NSAMP+1) T3=T3+0.1*(LOOP+LOOP2)
F      WRITE(NTERM,*) 'T3',T3
C   ** CALCULATION OF OBJECTIVE FUNCTION **
C   *** THE FIRST LINE CORRESPONDS TO MAXIMIZING AEP
```

```
C  *** THE SECOND LINE CORRESPONDS TO MINIMIZING ENVIR IMPACT
C      OBJ(LOOP)=-AEP/1000.
F      OBJ(LOOP)=ENVI/10.
F      WRITE(NTERM,*) 'LOOP: OBJ FUNCTION',LOOP,OBJ(LOOP)
C  ** STATISTICS **
F      IF (LOOP .EQ. NSAMP) THEN
F         SUMA=0
F         SUMS=0
C      ** OBJECTIVE FUNCTION AVERAGE **
F         DO 10 I=1,NSAMP
F           SUMA=SUMA+OBJ(I)
F           WRITE(NTERM,*) 'STAT OBJ FUNC',I,OBJ(I)
F 10      CONTINUE
F         EVNOBJ=SUMA/NSAMP
C      ** OBJECTIVE FUNCTION STANDARD DEVIATION **
F         DO 20 I=1,NSAMP
F            SUMS=SUMS+(OBJ(I)-EVNOBJ)**2
F 20      CONTINUE
F         SDEV=DSQRT(SUMS/(NSAMP-1))
F         WRITE(NTERM,*) 'AVERAGE & SDEV',EVNOBJ,SDEV
F         ICK=1
C      ** GENERATE THE WEIGHTING FUNCTION **
F         BT=0.001/(0.9**TLEV)
C      ** CALCULATE NEW OBJECTIVE FUNCTION **
F         EMNOBJ=EVNOBJ+2*BT*SDEV/(NSAMP**0.5)
F         IF (IN2 .EQ. 1) THEN
F            IN2=0
F            EMOBJ=EMNOBJ
F            GOTO 50
F         END IF
F         DELTA=EMNOBJ-EMOBJ
F         IF (DELTA .LT. 0) GOTO 30
F         W=DEXP(-DELTA/T)
F         WRITE (NTERM,*) 'DEXP',W
F         IF (W .GT. RDM()) GOTO 30
C      ** REJECT THE MOVE **
F         X1=X1OLD
F         X2=X2OLD
F         X3=X3OLD
F         Y1=Y1OLD
F         WRITE(NTERM,*) 'REJ: X1,X2,X3,Y1,EMOBJ,CS'
F         WRITE(NTERM,*) X1,X2,X3,Y1,EMOBJ,CS
F         GOTO 50
C      ** ACCEPT THE MOVE **
F 30      EMOBJ=EMNOBJ
F         NSA=NSAMP
F         ACC=ACC+1
F         CS=EVNOBJ
F         WRITE(NTERM,*) 'NSA',NSA
F         WRITE(NTERM,*) 'ACC',ACC
F         WRITE(NTERM,*) 'ACT: X1,X2,X3,Y1,EMOBJ,CS'
F         WRITE(NTERM,*) X1,X2,X3,Y1,EMOBJ,CS
F      END IF
F 50   ICK2=0
```

```
    EXECUTE AFTER BLOCK B2

TRANSFER T-1
    SET BLOCK-VAR BLOCK=B1 VARIABLE=TEMP SENTENCE=PARAM
    EQUAL-TO BLOCK-VAR BLOCK=B3 VARIABLE=TEMP SENTENCE=PARAM

CONVERGENCE C-2 WEGSTEIN
    TEAR 1

CONVERGENCE C-1 DIRECT
    TEAR 49
    PARAM MAXIT=9999

CONVERGENCE C-3 SECANT
    SPEC DS-1

SEQUENCE S-1 INIT C-1 B2 CONTROL U-ELEC U-STEH U-STEL U-WAT&
        U-WATCH C-2 HX1 DUP1 CSTR M1 HX5 PLUG M2 MX3 HX2  &
        ABS DR1 HX3 C-3 DR2 (RETURN C-3) CMP1 HX4 FL1 D1  &
        FL2 MX2 SPL CMP2 MX1 (RETURN C-2) D2 D3 E-1 E-2  &
        E-3 E-4 E-5 E-6 E-7 E-8 E-9 E-10 E-11 EI AEP STOC  &
        B3 T-1 B1 (RETURN C-1)

REACTIONS RSCH-1 POWERLAW
    REAC-DATA 1 PHASE=V
    REAC-DATA 2 PHASE=V
    REAC-DATA 3 PHASE=V
    REAC-DATA 4 PHASE=V
    RATE-CON 1 PRE-EXP=2.56E8 ACT-ENERGY=35260
    RATE-CON 2 PRE-EXP=6.28E7 ACT-ENERGY=30580
    RATE-CON 3 PRE-EXP=2.56E8 ACT-ENERGY=35260
    RATE-CON 4 PRE-EXP=2.93E8 ACT-ENERGY=37490
    STOIC 1 MIXED CH4 -1 / CL2 -1 / CH3CL 1 / HCL 1
    STOIC 2 MIXED CH3CL -1 / CL2 -1 / CH2CL2 1 / HCL 1
    STOIC 3 MIXED CH2CL2 -1 / CL2 -1 / CHCL3 1 / HCL 1
    STOIC 4 MIXED CHCL3 -1 / CL2 -1 / CCL4 1 / HCL 1
    POWLAW-EXP 1 MIXED CH4 1 / MIXED CL2 1
    POWLAW-EXP 2 MIXED CH3CL 1 / MIXED CL2 1
    POWLAW-EXP 3 MIXED CH2CL2 1 / MIXED CL2 1
    POWLAW-EXP 4 MIXED CHCL3 1 / MIXED CL2 1
```

VITA

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