THE DEVELOPMENT AND APPLICATION OF COMBINED WATER AND MATERIALS PINCH ANALYSIS TO A CHLOR-ALKALI PLANT

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ABSTRACT

Pinch Analysis, in the broadest sense, is concerned with the optimal use of resources (material or energy) in a multi-process system. Pinch Analysis based techniques have emerged for water systems over the past decade. A major assumption that has been made in applying these techniques is that a process system can be segregated into a set of process streams and a set of water streams. With this distinction in place, only the water streams are considered in the Pinch Analysis with the process streams represented implicitly. This approach has obvious limitations in situations where a clear distinction between process streams and water streams cannot be made.

The chlor-alkali process is an example of a system in which the clear distinction between process streams and water streams cannot be made. Water is intrinsically involved in the process, serving as a carrier medium for raw materials and eventually becoming part of the products produced by the complex. Hydrochloric acid and caustic soda are reagents which are both used within and produced by the complex. These reagents are required by the process at a range of concentrations and the concentrated reagent is diluted to the required concentrations using demineralised water. Within the chlor-alkali complex, a number of effluents containing the reagent species are available and are typically sent to drain. It is conceivable that these effluents might be recovered and used for dilution purposes instead of demineralised water. This would bring about a reduction in the amount of water and concentrated reagent used and the amount of effluent produced by the complex. Given the economic value of these reagents relative to water, their recovery, if feasible, is likely to dominate the optimal water-use and effluent generation strategy.

Current Water Pinch Analysis theory relies on the distinction being made between process streams and water streams and does not consider the recovery of reagents or the presence of desirable species within the system. In addition, the assumption is made that species are non-reactive; reactive species such as hydrogen chloride and sodium hydroxide, fall outside the scope of the current theory.

The objectives of this study have included the development of an approach which is able to address these limitations of the existing theory. This approach, termed Combined Water and Materials Pinch Analysis seeks to identify optimal use strategies for raw materials and reagents, in addition to water-use and effluent generation. The approach combines mathematical programming with conceptual insights from Water Pinch Analysis. The approach is based on the optimisation of a superstructure which represents the set of all possible flow configurations for water, reagents and raw materials between the various

operations within the process system; this problem is solved as a nonlinear programming (NLP) problem using standard optimisation tools.

The application of the developed approach to the Sasol Polymers chlor-alkali complex at Umbogintwini, south of Durban, has been a further objective of this study. Given the variety of process operations present within the complex, which differ both in terms of their physical structure and function, individual process models for these operations were required. These models were described in terms of four basic functional elements, namely, mixing, flow separation, component separation and reaction, and incorporated into the superstructure. Given the complexity of the problem, the process system was divided into three subsystems which were optimised in isolation from each other. These results were subsequently integrated to reflect the performance of the subsystems in combination with each other. The results showed a potential reduction of 14% in water-use and 42% in effluent production by the complex, relative to the existing operating configuration. Amongst other savings in material use, the results indicated a 0.2% reduction in the use of salt, a 1.6% reduction caustic soda use and an 8.3% reduction in the use of hydrochloric acid. Economically, the potential saving identified was R 945 727 per annum, based on operating costs in the year 2000.

The final objective of this study was the interpretation of the pinch as it relates to the Combined Water and Materials Pinch Analysis problem. A general definition of the pinch was proposed; according to this definition, the pinch corresponds to that constraint or set of constraints which limits the performance of the system, that is, prevents it from further improvement.   For the Combined Water and Materials Pinch Analysis problem, this performance is measured in terms of the operating cost. This definition is thus a departure from its usual thermodynamic interpretation of the pinch; in addition, the pinch is defined in terms of a constraint or a set of constraints instead of a point. These constraints are identified by an analysis of the marginal values provided by the optimisation algorithm. Marginal values are also used as a means of identifying process interventions which may be effected such that the performance of the system may be improved further.

PREFACE

I, Paolo Gianadda, declare that unless indicated, this thesis is my own work and that it has not been submitted, in whole or in part, for a degree at another University or Institution.

Paolo Gianadda
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ACKNOWLEDGMENTS

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COMPACT DISC

This thesis is accompanied by a CD which contains the spreadsheets of data used in this study. The GAMS coding for the various subsystems is also presented on this CD. A description of the files on the CD is presented in the file README.txt

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NOMENCLATURE

The nomenclature for this thesis is divided into two parts. The first part represents the nomenclature used in the literature from the field of water-reuse networks, as reported in **Chapter 2**. The second part is the general nomenclature which is used in the rest of the thesis.

NOMENCLATURE used in CHAPTER 2 - LITERATURE

C	contaminant concentration
$C_{apparent\ pinch}$	apparent pinch concentration prior to the inclusion of water losses and gains
C_e	environmental discharge concentration limit
$C_{i,k}^{in}$	concentration of contaminant k at the inlet of operation i
$C_{i,k}^{in,max}$	maximum inlet concentration limit for contaminant k in operation i
$C_{i,k}^{out}$	concentration of contaminant k at the outlet of operation i
$C_{i,k}^{out,max}$	maximum outlet concentration limit for contaminant k in operation i.
C^{in}	inlet concentration of contaminant
$C_{j,k}^{out}$	concentration of contaminant k at the outlet of operation j
C^{out}	outlet concentration of contaminant
C_p^{in}	contaminant concentration at the process inlet of an operation
C_{pinch}	pinch concentration
C_p^{out}	contaminant concentration at the process outlet of an operation
C_{regen}	concentration of contaminant from regeneration
CST_d	cost factor associated with the use of discharge point d
CST_w	cost factor associated with the purchase of source w
C_w^{in}	contaminant concentration at the water inlet of an operation
$C_{w,k}$	concentration of contaminant k associated with freshwater source w
C_w^{out}	contaminant concentration at the water outlet of an operation

NOMENCLATURE used in CHAPTER 2 - LITERATURE

$C_{1,B}$	upper concentration boundary for treatment operation 1
$f(x,y)$	objective function
F_d	total flow of water associated with wastewater discharge point d
$F_{i,d}$	flow from operation i to wastewater discharge point d
F_i^{in}	inlet water flow associated with operation i
F_i^{out}	outlet water flow associated with operation i
$F_{j,i}$	flow from operation j to operation i
F_w	water flowrate through an operation (Equation 2.1)
	total flow associated with freshwater source w (Equation 2.9)
$F_{w,i}$	flow of water from freshwater source w to operation i
$g(x,y)$	inequality constraint
$h(x,y)$	equality constraint
$K_{sp,CaSO4}$	solubility product for calcium sulphate
m	mass-load of contaminant transferred to water stream
m_T	total mass-load of contaminant removed in treatment
Δm	mass-load of contaminant transferred from the process stream to the water stream
Δm_T	mass-load of contaminant removed in treatment operation
$\Delta m_{i,k}$	mass-load of contaminant k transferred to the water over operation i
RR_l	contaminant removal ratio for treatment operation 1
x	continuous variable
y	discrete variable
Z	objective variable (Equation 2.3)
	operating Cost (Equation 2.14)

NOMENCLATURE used in CHAPTER 2 - LITERATURE

$[Ca^{2+}]$	molar concentration of calcium
$[SO_4^{2-}]$	molar concentration of sulphate

GENERAL NOMENCLATURE

A^-	anion
$c_{n,k}$	concentration of species k associated with stream n in process module
C_k	concentration of species k associated with the flow into a demand
C^{LIM}_k	limiting (maximum or minimum) concentration at a demand
$C^{LIM}_{j,k}$	limiting (maximum or minimum) concentration of species k associated with sink j
$C^{MAX}_{j,k}$	maximum concentration of species k associated with sink j
C^{MAX}_k	maximum concentration of species k permitted by a demand
C^{MIN}_k	minimum concentration of species k permitted by a demand
$C^{PSRC}_{h,k}$	concentration of species k in primary source h
$C^{REQ}_{j,k}$	required concentration of species k associated with sink j
C^{REQ}_k	concentration of species k required by a demand
$C^{SNK}_{j,k}$	concentration of species k associated with sink j
$C^{SSRC}_{i,k}$	concentration of species k in secondary source i
CST^{PSRC}_h	cost associated with the use of primary source h
CST_{RESIN}	resin replacement cost per regeneration
CST^{SNK}_j	cost associated with the discharge of flow into sink j
CST^{SSRC}_i	cost associated with the use of secondary source i
C_w^{in}	contaminant concentration at the water inlet of an operation (Equation 6.4)

GENERAL NOMENCLATURE

C_w^{out}	contaminant concentration at the water outlet of an operation (Equation 6.4)
ε	represents an infinitesimal change in the value of a constraint equation $g(x)$ (Equation 6.2)
f_n	mass flow associated with stream n in process module
f_{CS}	caustic soda requirement for regeneration associated with a particular operating configuration
$F_{CS,ec}$	quantity of caustic soda required for regeneration when the ionic load removed from the influent water is equivalent to the exchange capacity of the demineralisation plant
F^{PSRC}_h	total mass flow from primary source h
$F^{PSRCSNK}_{h,j}$	mass flow from primary source h to sink j
F^{SNK}_j	total mass flow to sink j
F^{SSRC}_i	total mass flow from secondary source i
$F^{SSRCSNK}_{i,j}$	mass flow from secondary source i to sink j
F_w	water flowrate through an operation (Equation 6.4)
HX	hydrogen form of cation-exchange resin
$g(x)$	constraint equation (Equation 6.1)
λ	marginal value (Equation 6.3)
LD	total ionic load removed from the influent water
LD_{ec}	exchange capacity of the demineralisation plant
$L_{i,j}$	lower limit for the mass flow between secondary source i and sink j
M	scalar multiplier which depends on the desirability of a species at a demand
$MM_{j,k}$	matrix of parameters describing the desirability of species k at demand j
M_k	molar mass of species k
MX	cation form of cation-exchange resin

GENERAL NOMENCLATURE

MX_2 divalent cation form of cation-exchange resin

M^+ cation

M^{2+} divalent cation

Δm mass-load of contaminant transferred to the water stream (Equation 6.4)

NaX sodium form of cation-exchange resin

$N_{i,max}$ maximum number of branches that secondary source i may be divided into

$N_{j,max}$ maximum number of branches which may combine to feed sink j

$N_{q,k}$ stoichiometric coefficient for species k in reaction q

r_q molar extent of reaction q in reaction block

S_n flow split ratio associated with branch n from flow separator

$S_{n,k}$ component split ratio associated with branch n from component separator

TC operating cost

$U_{i,j}$ upper limit for the mass flow between secondary source i and sink j

x   the set of variables adjusted during the course of the optimisation (Equation 6.1)

XA anion form of anion-exchange resin

XOH hydroxide form of anion-exchange resin

Z the constrained objective function as evaluated at the optimum (Equation 6.3)

$Z_{i,j}$ binary variable corresponding to the existence or non-existence of a mass flow between secondary source i and sink j

$[Ca^{2+}]$ molar concentration of calcium

$[CO_3^{2-}]$ molar concentration of carbonate

$[Mg^{2+}]$ molar concentration of calcium

$[OH^-$ molar concentration of hydroxide

GENERAL NOMENCLATURE

Subscripts

h	primary source
i	secondary source
j	sink
k	aqueous species
n	stream number in process module
q	reaction

Superscripts

LIM	limiting
MAX	maximum
MIN	minimum
PSRC	primary source
REQ	required
SNK	sink
SSRC	secondary source

ABBREVIATIONS

AECI   African Explosives and Chemical Industries

CD   Compact Disc

CS   Component Separator

Demin   Demineralised or demineralisation

DWAF   Department of Water Affairs and Forestry, South Africa

E   Effluent

FAO   Food and Agriculture Organisation of the United Nations

FS   Flow Separator

GAMS   General Algebraic Modelling System

GIS   Geographic Information System

HEN   Heat-Exchange Network

IDE   Integrated Development Environment

IXR   Ion-Exchange Regeneration

LIM   Limiting

LC   Liquid Chlorine

LP   Linear Programming

M   Mixer

MAX   Maximum

MBC   Membrane Cell

MEN   Mass-Exchange Network

MILP   Mixed-Integer Linear Programming

MIN   Minimum

MINLP   Mixed-Integer Nonlinear Programming

MIP	Mixed-Integer Programming
MSA	Mass-Separating Agent
NLP	Nonlinear Programming
PSRC	Primary Source
R	Reaction
REAMEN	Reactive Mass-Exchange Network
REQ	Required
RMINLP	Relaxed Mixed-Integer Nonlinear Programming
SNK	Sink
SSRC	Secondary Source
TDS	Total Dissolved Solids
TP	Treatment Process
UMIST	University of Manchester Institute of Science and Technology
UNEP	United Nations Environment Programme
UOS	Umbogintwini Operational Services
USEPA	United States Environmental Protection Agency
W	Water
WAP	Water/Wastewater Allocation Planning
WCAP	Wastewater Cleanup Allocation Planning
WIN	Waste Interception and Allocation Network
WRC	Water Research Commission of South Africa
WUTN	Water-Use and Treatment Network

GLOSSARY

active constraint | An equality constraint or inequality constraint which has reached its bound.

bilinear | A non-convex term in a mathematical equation which arises from the product of two variables, in this case, flow and concentration.

component separator block | An element of the process module which is used to represent component separations. The species concentration in each branch associated with a component separator block may be different.

composite curve | A graphical representation of the performance of the system. This is typically a plot of some quality factor versus some quantity factor.

concentration profile | The set of species concentrations by which sources and sinks may be characterised.

connection | A path along which material flows between a source and a sink in the process system.

connectivity matrix | A matrix of ones and zeros which correspond to the logical possibility of a connection between a particular source and a particular sink within the process system. This is used in the GAMS modelling to eliminate inappropriate matches from the superstructure considered by the optimisation.

constraint | A mathematical equation used to describe the performance of the process system in the optimisation model.

contaminant | Any property that prevents the direct reuse of water.

decomposition | An approach to dealing with large process systems in which the process system is divided into a number of smaller subsystems.

demand | The point at which water or other materials are required by the process system.

external sink | Used interchangeably with terminal sink. Represents a final destination for material flow.

external source | A source of water or material which is supplied from outside the process system. External sources are all primary sources.

flow separator block	An element of the process module which represents the deliberate division of a stream. The concentrations associated with each branch of the flow separator block are equal.
hold-up volume	A term used in the context of the regeneration sequences of the demineralisation plant and the cation-exchanger. This refers to the volume of fluid present in the ion-exchange bed at the point of change from one stage of the regeneration sequence to the next.
limit	Typically an inequality constraint which is used to describe a maximum or minimum condition which must be satisfied in the process system.
marginal value	This provides an indication of the sensitivity of the objective variable to an infinitesimal change in a constant in an active constraint. Used interchangeably with sensitivity.
match	Used interchangeably with connection. The path along which material flows from a source to a sink.
mixer	A conceptual element of the superstructure which represents the point at which sources combine to feed a particular sink.
mixing block	An element of the process module which represents the deliberate combination of water or material streams.
network configuration	The set of connections between sources and sinks which satisfies the production objectives of the process system.
non-convexity	A characteristic of a term in a constraint equation which is explained as follows: if two points on the boundary of the feasible region are connected by a straight line, all points along this path are not necessarily in the feasible region. Non-convex terms give rise to multiple optima in the solution space.
pinch	The constraint or set of constraints which limits the performance of the system under consideration.
primary source	A source for which the concentration profile is fixed.
process intervention	A process technology change which is effected to the process system.
process module	A model which represents a particular unit operation, group of unit operations or stage of a unit operation of the process system in the optimisation problem. Process modules comprise mixing, flow separator, component separator and reaction blocks.

process source	A source which is available from within the process system. Process sources may be either primary sources or secondary sources.
process system	A set of operations which effects the transformation of raw materials to products.
reaction block	An element of the process module which represents the transformation of species by chemical reaction.
regenerant	A term used to describe a reagent used in ion-exchange regeneration.
regeneration	In the context of ion-exchange, a term used to describe the elution of ions from the ion-exchange resin. In the context of water, a term used to describe a treatment operation which improves the quality of water such that is may be reused further.
secondary source	A source for which the concentration profile depends on the operation of the process module from which it emerges.
sensitivity	A term used interchangeably with marginal value. Represents the sensitivity of the objective variable to an infinitesimal change in a constant of an active constraint.
sink	A point at which material is consumed by the process system.
source	A point at which a supply of material is available to the process system.
splitter	A conceptual element of the superstructure which represents the division of a source into a number of branches which are routed to mixers of the superstructure.
subsystem	A subset of operations of the process system which arises from the application of a decomposition strategy to the process system.
superstructure	The set of inter-process flows between the various process operations within the process system and the flows to and from the external sinks and sources respectively.
supply	A source of material available to the process system. Used interchangeably with source.
terminal sink	A sink which is external to the process system. Represents a final destination for material flow. Used interchangeably with external sink.

1

INTRODUCTION

This thesis is concerned with the development and application of Combined Water and Materials Pinch Analysis to the chlor-alkali industry. This chapter introduces this topic and provides a context for this research. Section 1.1 examines the status of freshwater in South Africa and highlights the need for conservation-oriented approaches to water-use. Section 1.2 introduces the Cleaner Production philosophy and other related concepts. The way in which water is used in industrial systems is considered in Section 1.3. Section 1.4 provides an introduction to the field of Water Pinch Analysis while Section 1.5 considers the application of current Water Pinch Analysis theory to the problem presented by the chlor-alkali complex. The objectives of this study are presented in Section 1.6 while Section 1.7 provides the outline of this thesis.

1.1 THE STATUS OF WATER IN SOUTH AFRICA

The availability of an adequate supply of freshwater pervades all facets of modern-day society and is critical to long-term economic development, human health, social welfare, and environmental sustainability (Serageldin, 1996). South Africa is classified as a water-scarce country with approximately 65% of the country receiving an annual rainfall of less than 500 mm (FAO, 2002). It is however with this limited supply of freshwater that South Africa must satisfy, as best possible, all of its competing freshwater demands.

A recent analysis by the South African Department of Water Affairs and Forestry (DWAF) showed that in the year 2000, 11 of the 19 water management areas in the country were experiencing a water deficit (DWAF, 2002). In these areas, too much water was being used by some user sectors, to the extent that either the ecosystems in these catchments were placed under stress or other user sectors were unable to rely on their fair share of water. It is predicted that by the year 2025, even more water management areas will be facing a water deficit situation (DWAF, 2002).

One of the fundamental principles of the recently introduced National Water Act of South Africa (DWAF, 1998) is the sustainable management of the country's water resources. Here, the primary objective is to achieve long-term, and environmentally sustainable, social and economic benefits for society from the use of water (Leestemaker, 2001). In this framework,

water is considered to be a public good, with only the allocation of water for basic human and environmental needs receiving any priority. Other water users require authorisation to use water through the issuing of permits by the state. These permits are issued for limited time periods and are subject to renewal at the end of these periods.

Industry presently accounts for about 8% of the total amount of freshwater used in South Africa (DWAF, 2002). Other user sectors include agriculture (60%), domestic use (11%) and forestry (8%), with the balance being required to sustain the natural environment (13%). While agricultural and urban runoff constitute a greater source of pollution overall (Fry and Rast, 1996), industry produces an extensive range of pollutants and some of these are extremely hazardous to both humans and the natural environment, even at low concentration levels.

The recently proposed National Water Resource Strategy of South Africa (DWAF, 2002) recognises that water resource management must take place around both water quantity and quality. In a recent article on the challenges facing South Africa in terms of meeting its future water demands, it is noted that the cost of water in South Africa is higher only than that of Canada which enjoys a cheaper supply (Poggiolini, 2000). Johan Stoop, the demand manager for Rand Water at the time of the article commented that the water tariff in South Africa is not forcing people to conserve water. The cost of conserving water by minimising wastage and treating wastewater to a standard acceptable for internal reuse remains high relative to the cost of freshwater. Serageldin (1996) is of the opinion that the problem relates to water not being perceived as an economic good. As such, the conservation of water will only be achieved when the cost of water is set at a level which transforms it into a commodity worth saving (Fry and Rast, 1996).

With the predicted increase in freshwater demand in South Africa, the cost of freshwater is certain to increase as water resources come under increasing pressure. With more users having to use this limited supply of freshwater, industry can expect to see more stringent restrictions on the type and quantity of effluent it is able to discharge accompanying the increased discharge tariffs. These measures are however reactive in nature and the opinion is held that a proactive approach is also required to encourage industry to conserve water (Serageldin, 1996). Such an incentive structure should reward practices which encourage the efficient use of resources and promote measures that are proactive in pollution prevention rather than reactive in pollution management. In particular, this involves the adoption of Cleaner Production techniques such as waste minimisation through source reduction.

With a water crisis looming in the not too distant future, the availability of freshwater to sustain local industry and foster its growth is no longer a certainty. It is however believed that industry has an important role to play in overcoming the water crisis in terms of marshalling its technology and management skills to aid society in managing its water resources (Fry and Rast, 1996). Of course this can only be achieved by industry setting the example for other users to follow, and this involves implementing water conservation in the confines of its own operations.

1.2 CLEANER PRODUCTION AND RELATED CONCEPTS

The Cleaner Production philosophy represents a marked departure from previous attitudes to pollution prevention, which saw pollution problems being dealt with at the end-of-pipe stage. The formal definition of Cleaner Production, as defined by the United Nations Environment Programme (UNEP) (UNEP, 2002a), is given as:

> *The continuous application of an integrated preventative environmental strategy to processes, products, and services to increase the overall efficiency, and reduce risks to humans and the environment.*
>
> • *For production processes, Cleaner Production results from one or a combination of conserving raw materials, water and energy; eliminating toxic and dangerous raw materials; and reducing the quantity and toxicity of all emissions and wastes at source during the production process.*
>
> • *For products, Cleaner Production aims to reduce the environmental, health and safety impacts of products over their entire life cycles, from raw materials extraction, through manufacturing and use, to the "ultimate" disposal of the product.*
>
> • *For services, Cleaner Production implies incorporating environmental concerns into designing and delivering services.*

Cleaner Production therefore embodies a preventative approach to dealing with pollution. Instead of dealing with the pollution problem at the end-of-pipe stage, Cleaner Production addresses the problem by preventing or minimising the amount of pollution created in the first instance (source reduction).

Amongst the concepts related to Cleaner Production, both Pollution Prevention and Waste Minimisation bear mentioning. Pollution Prevention is a term which is used interchangeably with Cleaner Production; like Cleaner Production, it aims to reduce pollution and environmental impact through source reduction (UNEP 2002b). Waste Minimisation is a concept introduced by the United States Environmental Protection Agency (USEPA) and is defined as *the on-site source reduction of waste by changes of input raw-materials, technology changes, good operating practices and production changes* (UNEP 2002b).

While many waste minimisation strategies exist, most of these are based on a combination of heuristics and experience. The success of these techniques is therefore subjective since decisions are made on an *ad hoc* basis and the pollution prevention strategies proposed by these methods are not necessarily optimal. One exception to this is the field of Process Integration. Unlike many other methods, Process Integration recognises that a chemical process system is a

highly integrated system of interconnected process units and streams and treats it as such. Rossiter (1994) points out that the philosophies of Cleaner Production and Process Integration are complementary to each other in that Process Integration techniques are inherently *conservation-oriented* in terms of enhancing the efficiency of the process through the efficient use of energy and materials.

El-Halwagi (1997) defines Process Integration as *a holistic approach to process design, retrofitting, and operation which emphasises the unity of the process*. The definition continues that *Process Integration provides a unique framework for fundamentally understanding the global insights of the process, methodically determining its attainable performance targets, and systematically making decisions leading to the realisation of these targets.* With this approach, it is possible to design new processes and retrofit existing processes that operate more efficiently and economically while simultaneously minimising the level of pollution produced by the process system.

One of the areas falling under Process Integration is that of Pinch Analysis, the application of which is one of the primary objectives of this thesis. Specifically, the application of Pinch Analysis to the rational management of water and effluent in a chemical complex is considered. However, before introducing this topic, it is necessary to consider the ways in which water is used within the industrial complex and how it might be used more efficiently.

1.3 INDUSTRIAL WATER-USE

Mann and Liu (1999) describe the typical water-use pattern for the process industry. After preliminary water treatment, water is distributed to three types of users within the process system: process users, utility users and other users. In progressing through the process system, the water may become contaminated with environmental pollutant species and emerges from the various users as wastewater. Wastewater is collected and treated in a centralised effluent treatment facility. Treated effluent emerges from the treatment facility and is discharged to the environment. The schematic layout of these operations is illustrated in Figure 1.1.[1]

Apart from introducing process changes which bring about a reduction in the inherent demand of a process system for freshwater, the reuse of water is widely recognised as a route to reducing the amount of freshwater used and wastewater produced by a process system (Rabb, 1970; Santhanam, 1972; Takama et al., 1980; Wang and Smith, 1994, Dhole et al., 1996). This implies using a certain quantity of water in the process system more than once, which in turn suggests the use of a certain quantity of water for which the quality is lower than that of freshwater. This quality is typically expressed in terms of the mass-load of species carried by the water and in most cases it is the presence of these species which prevents or limits the

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[1] *With regard to the schematic diagram presented in Figure 1.1, it bears mentioning that this situation represents an extremity which is unlikely in the South African context. Water is known to be scarce and a certain level of reuse is probably exercised in many process systems already; however, most systems are likely to conform to the schematic to some degree. It is probably also increasingly old-fashioned in the US and European contexts.*

widespread reuse of the water (Santhanam, 1972). These species are therefore undesirable from a water-reuse perspective and are termed contaminants.
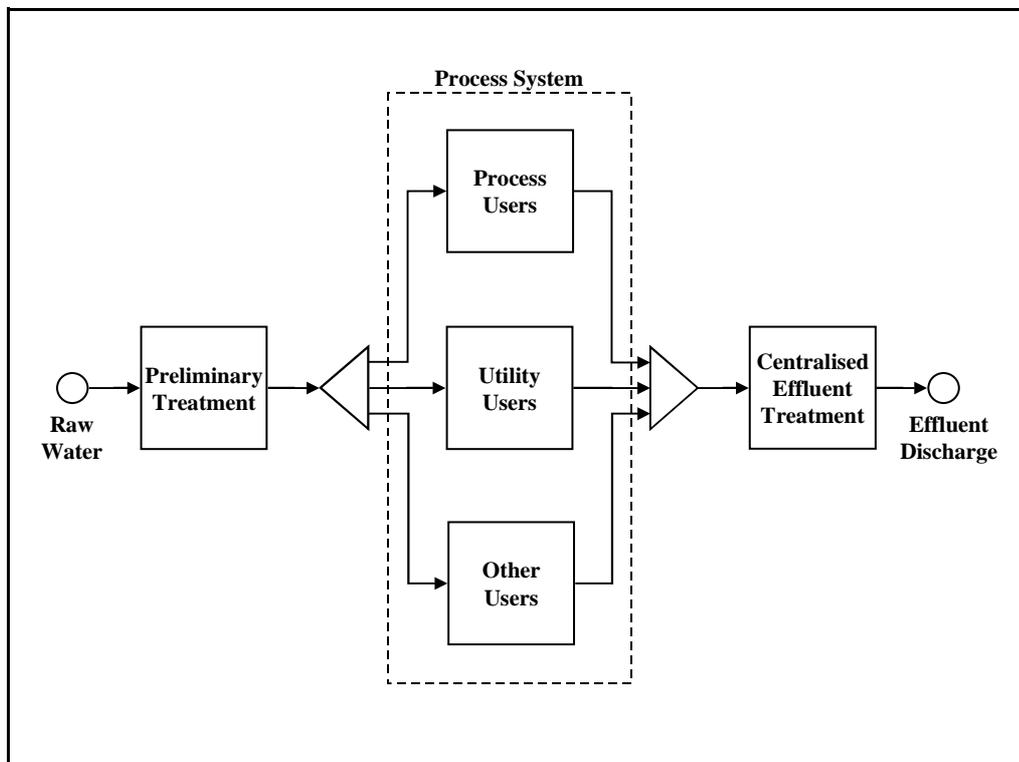
Figure 1.1. *Schematic diagram of water-use in the process industry (Smith (1995) referenced in Mann and Liu, (1999)).*

In order to maximise the reuse of water within the process system (and thereby minimise the amount of freshwater used and wastewater generated), it is necessary to identify which water-users are able to accept and use water of a quality which is inferior to that of freshwater. As such, each water-using operation may be characterised by a minimum water quality it requires for efficient operation. This implies that a process is able to accept water of this quality, or superior, to satisfy its water demand.

In terms of maximising the reuse of water, it is also necessary to consider the way in which the wastewater from the various water-users is collected (Nelson, 1990; Douglas, 1992). In process systems featuring once-through water-use, all of the wastewater is collected into a common stream, which progresses to the centralised effluent treatment facility. However, the quality of wastewater produced by the various water-users is different; for example, process condensate will have a quality which is superior to that of boiler blowdown. By mixing these two streams to produce a wastewater stream of intermediate quality and larger volume, two opportunities are missed. Firstly, from the water-use side, the condensate could be recovered and reused within the process system instead of being mixed with the blowdown effluent source and sent to the effluent treatment facility. This results in a reduction in the amount of freshwater required by the process system. Secondly, from the wastewater generation side, the

reuse of the process condensate will result in the production of a lower volume of effluent requiring treatment. Since the costs associated with effluent treatment tend to be strongly volume dependent, reducing the volume of wastewater requiring treatment is economically attractive since effluent treatment facilities can be smaller in size. Moreover, from a contaminant mass-load perspective, it is more cost-effective to treat a concentrated effluent than a dilute effluent containing the same contaminant mass-load (McLaughlin et al., 1992).

The segregation of effluent streams further affords the possibility of using a distributed effluent treatment facility rather than a centralised facility. Given that wastewater sources contain different levels and types of contaminant species, and that a series of treatment steps is usually required in dealing with these different species, distributed effluent treatment offers a means of treating only those wastewater streams which require treatment for a particular species rather than the entire effluent. Hence a portion of the effluent is treated in a particular treatment step while the remainder bypasses that step. This results in lower treatment costs and smaller treatment facilities. Figure 1.2 illustrates the difference between a centralised effluent treatment facility and a distributed effluent treatment facility.
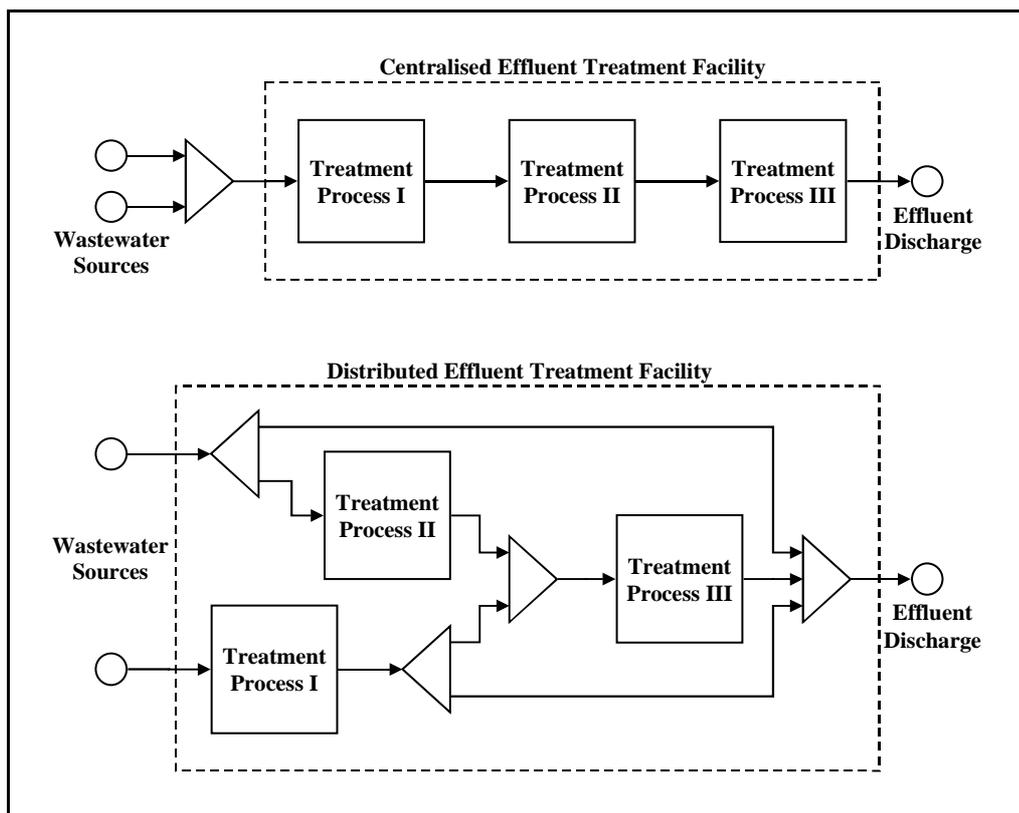
Figure 1.2. *Schematic diagram of a centralised effluent treatment facility and a distributed effluent treatment facility illustrating the differences between the two systems.*

Until this point, much of the discussion has focussed on the reduction of the volume of freshwater used and wastewater generated by a process system. Aside from the undesirable

contaminants present in the wastewater which limit the extent of water-reuse, certain useful species may also be present in the water; these species are typically reagents and raw materials which are used within the process system. However, through the typical practice of combining and routing all wastewater streams to the effluent treatment facility, opportunities for recovery of these species are lost.

In general, raw materials and reagents have a higher economic value than freshwater. Hence, the routing of these species together with the combined effluent stream to the effluent treatment facility represents an economic loss to the industry concerned prior to anything being spent on treating these species for pollution abatement purposes. Moreover, these species tend to have high environmental impacts, for the very reason that they are used in the industrial process, namely that they have a high chemical affinity. Proactively, seeking reuse opportunities for these streams and interception prior to their mixing with the combined effluent can yield significant economic benefits through a lower effluent volume requiring treatment and improved use of raw materials and reagents within the process system. In addition, the effluent load delivered to the effluent treatment facility is reduced which brings with it further economic benefits.

To date, all literature on the design of water-use systems has addressed the issue of minimising the volume of freshwater used and wastewater generated by a process system but less consideration has been given to the simultaneous minimisation of the effluent load. The work presented in this thesis, by virtue of the case study considered which involves water acting as a carrier medium for both reagents and raw materials, addresses both the minimisation of freshwater and wastewater volume and the effluent load.

1.4 WATER PINCH ANALYSIS

A novel view of Pinch Analysis, in the broadest sense, is that it is concerned with the optimal management of resources, whether they be material or energy, in a multi-process system. Pinch Analysis originally developed as a tool for the design of energy-efficient heat-exchange networks during the late 1970s and early 1980s in response to the sharp increase in the price of energy. Since then, Pinch Analysis based techniques have found application in a wide range of fields, including distillation column profiling, low-temperature process design, batch process integration, emissions targeting and water and wastewater minimisation; a recent overview of the field is provided by Linnhoff (1993).

In its original exposition, one of the principal characteristics of Pinch Analysis is the prediction of realistic performance targets which are independent of the structure of the final design (Linnhoff and Flower, 1978; Linnhoff et al., 1994). These performance targets, which in the case of Heat-Exchange Network (HEN) Synthesis extend to the minimum heating and cooling utilities required by the system, are predicted prior to any design work being carried out. Designs which achieve the predicted performance targets are subsequently formulated.

A further characteristic of the original exposition of Pinch Analysis as it pertains to the synthesis of heat-exchange networks is the so-called pinch point (Linnhoff et al., 1994). For heat-exchange between two fluids, thermodynamic equilibrium is established when a zero temperature difference or driving-force exists between the fluids exchanging energy. This situation corresponds to the maximum possible level of heat-exchange between the two fluids (which minimises the amount of external utilities required by the overall system) but requires a heat-exchanger of infinite heat-exchange area, and therefore capital cost. As a trade-off between the capital cost (heat-exchanger area) and operating cost (external utilities) a minimum temperature driving-force between the hot and cold streams in the heat-exchange network is defined. The so-called pinch point then corresponds to the region in the heat-exchange network where this minimum temperature driving-force is realised and thus represents the overall thermodynamic bottleneck for heat transfer in the heat-exchange network.

Hence, in its basic exposition, Pinch Analysis comprises two distinct stages - targeting followed by design, with the pinch point representing a purely thermodynamic bottleneck for the system. As such it is possible to achieve these objectives with the graphical tools upon which the initial exposition of the approach is based.

The application of Pinch Analysis based techniques to the minimisation of freshwater-use and wastewater generation in the process industry came to the fore in 1993 (Wang, 1993). This work represents an extension of the work on Mass-Exchange Network (MEN) Synthesis (El-Halwagi and Manousiouthakis, 1989), which in turn is an extension of the HEN Synthesis theory (Linnhoff and Flower, 1978; Linnhoff et al., 1994), to systems involving water. In this initial work, graphical tools are used for targeting the minimum water flowrate for a system of water-using mass-exchange operations with the design being carried out subsequent to the prediction of the freshwater target. The pinch point in this case corresponds to the region of the network at which a predetermined minimum concentration driving-force for the mass-transfer of contaminant species to the water has been reached.

Since this initial Pinch Analysis based approach, the design of water-reuse networks has been the subject of extensive research (Bagajewicz, 2000). Notably however, the use of graphical techniques for predicting the minimum freshwater requirement for a system has been shown to be somewhat limited in terms of the number of species and the types of water-using operations that can be considered. As a result, the use of mathematical programming or optimisation based approaches has become the preferred method for designing water-reuse networks. In addition to allowing the incorporation of multiple contaminants and different water-using operations, mathematical programming methods allow the incorporation of more complicated constraints such as forbidden or enforced connections in the network structure. While mathematical programming is currently the approach of choice for water-reuse network design, its use for this purpose was presented by Takama et al. (1980) over a decade before Wang's Pinch Analysis based approach.

One fundamental difference with the use of mathematical programming as opposed to Pinch Analysis is that the distinction between the targeting and design phases no longer exists with these being carried out simultaneously. In addition, the so-called pinch point may correspond or arise due to some other constraint, for example, an enforced connection within the network, rather than a thermodynamic bottleneck in the system. As a result, there is some debate as to whether mathematical programming approaches may be referred to as Pinch Analysis and the distinction between the two is often made (Rossiter, 1995). However, the present trend sees the incorporation of insights from Pinch Analysis into the mathematical programming approach. These insights involve the generation of a set of graphical system representations which provide an overall view of the performance of the system.

The term Water Pinch Analysis itself has become popularised through the availability of Linnhoff March's commercial software package WaterTarget^{TM} with its Pinch Analysis module WaterPinch^{TM} (Linnhoff and Tainsh, 1996). Academically too, the use of mathematical programming in conjunction with insights from Pinch Analysis is gaining recognition as Water Pinch Analysis (Alva-Argáez, 1998). As such, the work presented in this thesis follows this trend, that is, combining the two approaches.

Mann and Liu (1999) see Water Pinch Analysis as one of three tasks. According to their definition, Water Pinch Analysis involves the identification of the minimum freshwater and wastewater targets for the system while the design of the network which achieves these targets is termed Water Pinch Synthesis. The third task, Water Pinch Retrofit, involves the modification of an existing water-use network such that water-reuse is maximised through the introduction of effective process changes.

Related to the definition of Water Pinch Synthesis is that of Process Synthesis. Grossmann (1996) states the Process Synthesis problem as follows:

> *Given the specifications of input and of output streams - which may correspond to raw materials and desired products in flowsheets or simply to process streams in subsystems - the problem consists in integrating a process system that will convert the inputs into desired outputs so as to meet desired specifications while optimising a given objective or goal function.*

Seemingly, the efficient use of water and the minimisation of wastewater generation are encompassed by the definition of Process Synthesis. However, a further aspect of Water Pinch Analysis, and Pinch Analysis as a field, is the provision of powerful insight into the performance or behaviour of the system and how changes can be made such that additional improvements can be achieved (Linnhoff, 1993; Linnhoff et al., 1994; Buehner and Rossiter, 1996). This aspect is beyond the scope of Process Synthesis.

1.5 WATER PINCH ANALYSIS AND THE CHLOR-ALKALI COMPLEX

The problem presented by the chlor-alkali system is not a typical Water Pinch Analysis problem as reflected by current theory. One of the main characteristics of current Water Pinch Analysis theory is that the system may be segregated into a set of so-called process streams and a set of water streams. As such, only the water-side of the problem is considered explicitly in the Pinch Analysis with the process-side being represented implicitly. The situation presented by the chlor-alkali complex is one in which water acts as a carrier medium for the raw materials used and the products produced by the facility. It is therefore a process stream as well as a water stream and the distinction required by classical Water Pinch Analysis theory is not possible.

The species carried by the water add further complexity to the problem, both by their nature and their function. The products produced by the chlor-alkali complex include the reagents caustic soda and hydrochloric acid, both of which are also used within the process. Unlike the contaminants which are undesirable, these reagent species are useful and have a specific function in the process system. Using freshwater, these reagents are diluted from their supply strength to the various strengths required by different areas of the process system. Within the complex a number of effluent sources containing these reagent species are available and could substitute for some portion of the fresh concentrated reagent which is presently used to satisfy all of the reagent demands, thereby resulting in savings in both reagents and freshwater. Given the economic value of the reagents relative to water, the reuse and recovery of these reagents is extremely desirable and potentially more so than identifying the network design configuration which uses the smallest amount of water. Hence, in addition to considering the optimal use of water, the focus of the traditional Water Pinch Analysis problem, allowance must be made for the reuse and recovery of these different reagents. In fact, in light of these considerations, it is questionable whether the task at hand can be considered a Water Pinch Analysis problem at all.

A further characteristic of the species involved in the chlor-alkali system is their reactivity and the way in which they interact with other species. Current Water Pinch Analysis theory deals only with non-reactive contaminants. With these interactions being an intrinsic part of the chlor-alkali system, it is however necessary to consider these effects in formulating the optimal water and reagent use strategy.

1.6 PROJECT OBJECTIVES

This project is a component of a larger project entitled *The Application of Pinch Technology to the Rational Management of Water and Wastewater in an Industrial Complex* (WRC Project No. 851) (Brouckaert and Buckley, 2002) and the follow-up project *The Further Application of Pinch Analysis for Water and Effluent Management* (WRC Project No. 1158) funded by the

Water Research Commission of South Africa (WRC). Part of the objectives of the initial WRC project included the application of Water Pinch Analysis to various industrial sites, with an assessment of its applicability to the various situations encountered. The application of Water Pinch Analysis to the Sasol Polymers chlor-alkali complex located at Umbogintwini, south of Durban, South Africa, is thus a central objective of this project.[1] In applying Water Pinch Analysis to the complex, the specific aims are:

- The provision of an assessment of the suitability of the current techniques and tools in dealing with the situation presented by the chlor-alkali complex; this includes the presence of desirable and reactive species

- Given the limitations in the existing theory already highlighted in this chapter, the development of an approach that it is able to deal with:
  - it not being possible to differentiate between so-called process streams and water streams in some situations in the complex
  - the presence of desirable species in the system and the optimal use of reagents and raw materials in addition to freshwater
  - reactive species

- The application of this approach to determine the cost optimal strategy for water, reagent and raw material use and effluent generation at the chlor-alkali complex

- The assessment of the significance of the pinch for the situation involving desirable and undesirable species, some of which are of a reactive nature.

1.7 THESIS OUTLINE

Chapter 1 provides an introduction to the research project presented in this thesis. The scope and context of the work is outlined and the specific approach defined. In particular, some of the shortcomings of the existing theory in dealing with the situation presented by the chlor-alkali complex are highlighted.

Chapter 2 aims to establish the various key concepts used in this study and presents alongside these concepts a review of the relevant literature. This review begins with an examination of the conceptual approaches and progresses through to the use of mathematical programming for the design of water-reuse networks.

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[1] *During the course of this study, the Sasol Polymers chlor-alkali complex ceased operation at Umbogintwini due to logistical reasons (April 2001). However, all the required data for the completion of the study had been assimilated by this date and the closure of the complex therefore does not influence the results of the study.*

Chapter 3 provides an assessment of the suitability of the existing theory on Water Pinch Analysis to the situation presented by the chlor-alkali complex. The chlor-alkali complex is introduced in greater detail and the results and findings of a previous Water Pinch Analysis study (Gardner, 1999) are reviewed. The conceptual ideas behind Utility-Water Pinch Analysis and Process-Water Pinch Analysis are introduced as enhancements to the Water Pinch Analysis ideology. Finally, the Combined Water and Materials Pinch Analysis methodology is introduced.

Chapter 4 develops the methodology for Combined Water and Materials Pinch Analysis. The use of mathematical programming tools for the solution of this problem is considered and the mathematical model developed. The approach utilises a modular structure in which process modules are incorporated into a general superstructure of the network.

Chapter 5 considers the application of Combined Water and Materials Pinch Analysis to the problem presented by the chlor-alkali complex. The decomposition of the system into three subsystems is motivated and the modelling of the various process modules associated with these subsystems is discussed.

Chapter 6 presents the results obtained from the application of Combined Water and Materials Pinch Analysis to the chlor-alkali complex. The chapter begins with an interpretation of the significance of the pinch as it pertains to Combined Water and Materials Pinch Analysis. The results obtained from the optimisation of the various subsystems in isolation from each other are then considered in terms of three aspects. Firstly, the proposed network configuration is considered. The solution provided by the optimisation is then analysed such that insight is provided into which process interventions should be made to the system to enhance its performance further. Lastly some consideration is given to the implementation of the identified reuse strategy. Having considered each of the subsystems in isolation from each other, attention shifts to their functioning in combination with one another. Finally, a comparison is drawn between the results achieved for the chlor-alkali complex using Combined Water and Materials Pinch Analysis, those obtained from the initial study carried out by Gardner (1999) and those which would be achieved from the application of standard Water Pinch Analysis tools and theory.

Chapter 7 brings this investigation to a close with conclusions and recommendations from the study.

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2

LITERATURE

A significant amount of research has been carried out in the field of industrial water system design; this chapter presents a conceptual review of this field. Section 2.1 presents some of the basic concepts from the field and outlines the structure of this review in greater detail. There are three general approaches to water system design; these are conceptual approaches, heuristic and algorithmic approaches, and mathematical programming. The conceptual approaches developed from the field of mass-exchange networks and the coinciding link between this area of research and that of water system design is reviewed in Section 2.2. Section 2.3 reviews the conceptual approaches while the heuristic and algorithmic approaches to water system design are reviewed in Section 2.4.   The use of mathematical programming for water system design is reviewed in Section 2.5. Section 2.6 reviews the work which has been carried out in the field of combined resource system design. The optimisation of systems involving desirable and/or reactive species is reviewed in Section 2.7. Finally, some concluding comments on this chapter are presented in Section 2.8.

It is noted that due to difficulties in reconciling the different notations of the various authors, a special section, which pertains specifically to the notation presented in this chapter, is included in the Nomenclature section at the start of this thesis.

2.1 BASIC CONCEPTS IN EFFICIENT WATER-USE SYSTEM DESIGN

This section establishes some of the basic concepts in efficient water-use system design. It is around these concepts that the remainder of the review is structured. **Section 2.1.1** considers the overall problem associated with water minimisation while the various routes to minimising the amount of water used in an industrial process are considered in **Section 2.1.2**; factors which inhibit the reuse of water are considered in **Section 2.1.3**. **Section 2.1.4** presents the various conceptual models for industrial water-systems while **Section 2.1.5** outlines the different approaches to water-system design. The structure of the remainder of this review is considered in **Section 2.1.6**.

2.1.1 Water Minimisation - The Overall Problem

According to Takama et al. (1980a) the overall problem associated with reducing the amount of freshwater used by an industrial complex, and consequently the amount of wastewater generated by that complex can be divided into two complementary problems. One of these problems, referred to by the authors as the water planning problem, is associated with the optimal allocation of water to the water-using and wastewater treating units within the process system. The complementary problem, referred to as the water design problem, involves determining the optimal process conditions in these units for a given water allocation. In their research, Takama et al. make the assumption that the process conditions are optimal and consider only the first problem. This assumption is implicit in all subsequent research in the field.

2.1.2 Routes to Water Minimisation

Several authors have recognised water-reuse and process changes as two routes to reducing the amount of freshwater used by a process system (Rabb, 1970; Santhanam, 1972; Takama et al., 1980a; Wang and Smith, 1994a; Dhole et al., 1996). Within this definition of reuse, Rabb, Santhanam, Takama et al. and Dhole et al. include the possibility of water-reuse which is either direct or indirect following wastewater treatment. Wang and Smith (1994a) differentiate between these reuse patterns and include the following categorisations on reuse:

- Reuse - wastewater is reused directly within the process system subject to its quality being acceptable to operations within the process system.

- Regeneration Reuse - wastewater is partially treated to remove contaminants, the presence of which currently limits the reuse of the water. This water is reused in operations in which it has not previously been used.

- Regeneration Recycling - contaminants are removed from the wastewater via regeneration. This water is allowed to enter operations in which it has previously been used.

A term sometimes used interchangeably with regeneration is interception (El-Halwagi et al., 1996; Dunn and Wenzel, 2001; Dunn et al., 2001). By interception, El-Halwagi et al. refer to the use of a mass-exchange operation, for example, an absorber, for the selective removal of a particular species from a species-laden stream. Dunn and co-workers (Dunn and Wenzel, 2001; Dunn et al., 2001) consider a more general definition of the term interception. These authors equate it to the use of a technology which will allow the recycling and reuse of a wastewater stream at a particular location in the process system once the composition of the water has been reduced to a level acceptable to the receiving operation. This definition therefore encompasses that of El-Halwagi et al..

Two concepts related to water minimisation are System Closure and Zero Discharge. System Closure is a term which finds use particularly in literature from the paper industry (Sorin and Bédard, 1999b; Bédard and Sorin, 2000; Shafiei et al., 2001; Jacob et al., 2002). Jacob et al. explain that the objective of System Closure is to minimise the freshwater consumption and wastewater discharge to the environment by a process system. Goldblatt et al. (1993) consider the various definitions of Zero Discharge. Literally taken, Zero Discharge implies that no waste is produced by the process system; a situation that corresponds to an ideal and physically impossible process. Other definitions of Zero Discharge include the elimination of priority pollutants, toxic substances or even liquid effluent from the process system. Zero liquid discharge has been given specific consideration by Dericks et al. (2001). A more flexible description of Zero Discharge however extends to a process system producing a volume of wastewater which may not necessarily be small, but remains safe and benign to the receiving environment. In practice, it is concluded that the complete elimination of all waste in an existing process system is prohibitively costly. Some reduction in the level of waste production by the process system, through the low cost options of reuse and recycling, is however possible. An example of zero liquid discharge through a symbiotic relationship between industries is provided by Brouckaert et al (2001). In this example, a coal fired power station uses effluent from the affiliated coal mine as part of its water make-up, while all effluent from the power station is used to suppress dust on the mine dumps.

2.1.3 Factors Inhibiting Water-Reuse

The quality of wastewater in terms of the species it carries is recognised universally as the primary factor which limits the extent to which wastewater can be reused within the process system (Rabb, 1970; Bishop and Hendricks, 1971; Santhanam, 1972; Pingry and Shaftel, 1979; Takama et al., 1980a; Ocanas and Mays, 1981; Nelson, 1990; Wang and Smith, 1994a). These species are recognised as pollutants or contaminants, the presence of which is undesirable. More specifically, a contaminant is defined as being any property that prevents the direct reuse of wastewater (Linnhoff March Limited, 2001). In general, the contaminant species considered in the literature and the water-use network design tools presently available have the attributes that they are of a non-reactive nature, that they blend linearly with each contaminant obeying the conservation of mass, and that they have linear measurement units (Linnhoff March Limited, 2001). pH is a nonlinear quality measurement which cannot be represented in water-use network design since it disobeys the linear mixing rules; it may however remain a decisive factor in determining the reusability of a water source at a particular location practically. It should be noted that the assumption of a dilute system is universally applied. As such, the mass of the contaminant is considered insignificant relative to that of the mass of water and its contribution is thus ignored. A workaround for this is however noted by El-Halwagi and Manousiouthakis (1989).

Recognition of desirable species carried by the water is given by a number of authors (El-Halwagi et al., 1992; Ostfeld and Shamir, 1992; Smith and Petela, 1992b; Gardner, 1999; Sorin and Bédard, 1999b; Baetens and Tainsh, 2000; Bédard and Sorin, 2000; Shafiei et al.,

2001; Brouckaert et al., 2002; Jacob et al., 2002). Consideration of reactive species is given by a few authors (El-Halwagi and Srinivas, 1992; Srinivas and El-Halwagi, 1994a; Warren et al., 1995; Gardner, 1999; Huang et al., 1999b; Brouckaert et al., 2001). The approach to dealing with these reactive and desirable species will be considered further in **Section 2.7**.

It should be noted that in practice, the overall quality of a water source is expressed in terms of many quality factors. In the context of water-use system design, Wang and Smith (1995a) caution against the inclusion of too many contaminants into the analysis since the intention is not to simulate the process system, but only to represent those factors which prevent water-reuse; this is considered a key concept. It is therefore sometimes possible to represent the system entirely in terms of a single contaminant species. Where this is not possible, it is necessary to represent multiple contaminant species. Problems involving multiple contaminants are of a higher dimensionality than those for single contaminants; the solution methods are correspondingly different and more complex for multiple contaminants. Aggregated contaminants such as total dissolved solids (TDS) allow the consideration of multiple quality factors using a single contaminant approach (Sorin and Bédard, 1999b; Bédard and Sorin, 2000). Consideration of both single contaminant and multiple contaminant approaches will be presented in more detail within this review.

The use of entropy as an indicator of the reuse potential of water is considered by Thomas et al. (2000).

2.1.4 Conceptual Models for Water Systems

One conceptual model of the process system in the context of waste minimisation is the so-called Onion Diagram which was conceived by Linnhoff and co-workers and the first representation of which appeared in 1982 (Linnhoff et al., 1994). In their attempt to provide a structured approach to putting waste minimisation into practice in the process industry, Smith and Petela (1991a,b; 1992a,b,c) present the Onion Diagram as a representation of the hierarchy of the components of a chemical process (Figure 2.1). The chemical reactor resides at the core of the *onion* and the design of this component determines the separation and process recycle problem which forms the second layer of the *onion*. These two layers determine the material and energy balances of the system and allow the design of the heat recovery system which makes up the third layer. Having exploited all of the opportunities for heat recovery, utilities are added to close the system energy requirement and the utility layer makes up the outer layer of the *onion*. Two classes of waste are identified, namely process waste, which originates from the two core layers, and utility waste, which originates from the two outer layers. Process waste comprises waste by-products and purge streams while utility waste includes flue gas and ash from fuel combustion and waste from boiler feed treatment and boiler blowdown.

In the context of water minimisation, two conceptual models have been presented. The difference between the two models relates to the way in which the treatment of the wastewater is viewed. Kuo and Smith (1998a) represent the water system as being composed of three interacting subsystems, namely the water-using subsystem, the regeneration subsystem and the

wastewater treatment subsystem (Figure 2.2a). Huang et al. (1999b) and Benkő et al. (2000) comment that while water treatment processes may differ according to their role being end-of-pipe treatment or regeneration, both roles are common in effecting the removal of contaminants from the wastewater they treat. As a result, these authors do not consider a distinction between the regeneration and wastewater treatment subsystems and represent the water system as being composed of a water-using subsystem and a wastewater treatment subsystem (Figure 2.2b). A similar view is held by Takama et al. (1980a), Alva-Argáez (1999) and Brouckaert et al. (2001).
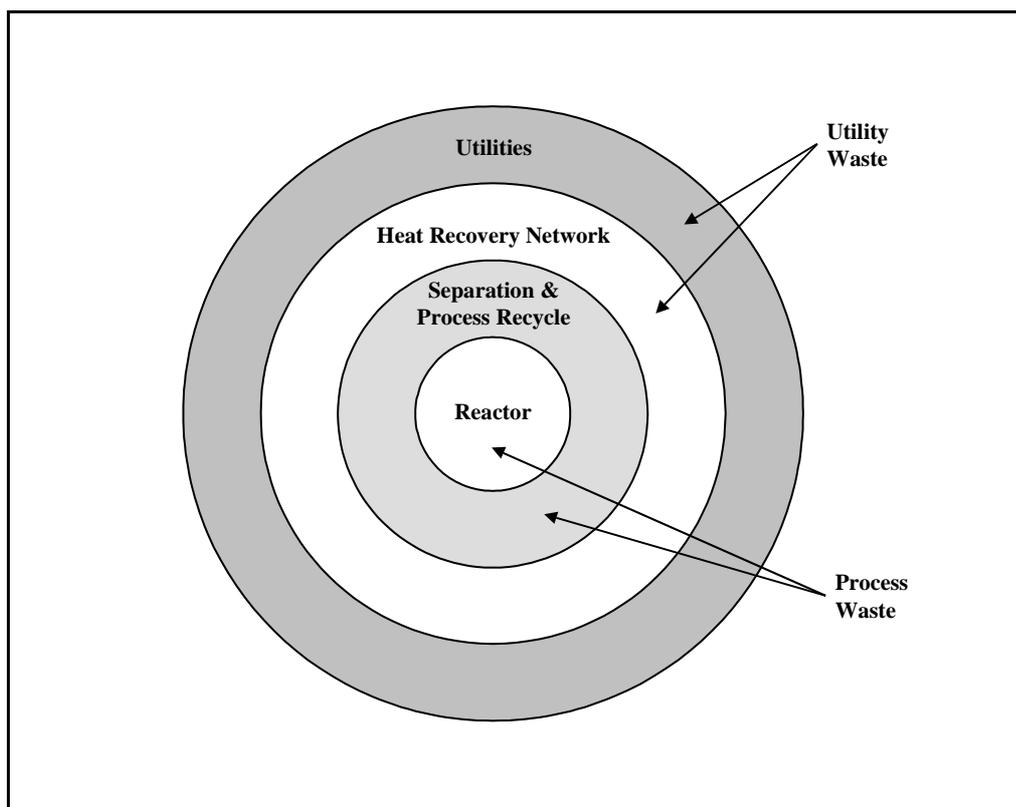
Figure 2.1. *The Onion Diagram as a conceptual model of the hierarchy of the components of a chemical process (Smith and Petela, 1991a).*

Different approaches exist in terms of handling the interactions between these different subsystems in the overall design of the water system. Wang and Smith (1994a) see the task of water management as being made up of two tasks. The first task involves minimising the amount of freshwater used, and therefore wastewater generated, by the process system through water-reuse and regeneration. The second task, which is distinct from the first, involves treating the generated wastewater to an acceptable discharge standard, with the objective being to minimise the overall treatment cost. A significant majority of the work in the field carries this distinction with researchers either considering only the first task or only the second (Bagajewicz, 2000). A few authors consider both tasks simultaneously (Takama et al., 1980a,b; Alva-Argáez, 1999; Huang et al., 1999b; Brouckaert et al., 2001). The problem associated with the design of the water-use system is also referred to as the Water/Wastewater

Allocation Planning (WAP) problem (Bagajewicz and Savelski, 2001) while the wastewater treatment problem is referred to as the Wastewater Cleanup Allocation Planning (WCAP) problem (Bagajewicz and Savelski, 2001). Huang et al. (1999a,b) refer to the problem in which the water-using and water treating operations are considered simultaneously as the Water-Use and Treatment Network (WUTN) problem.
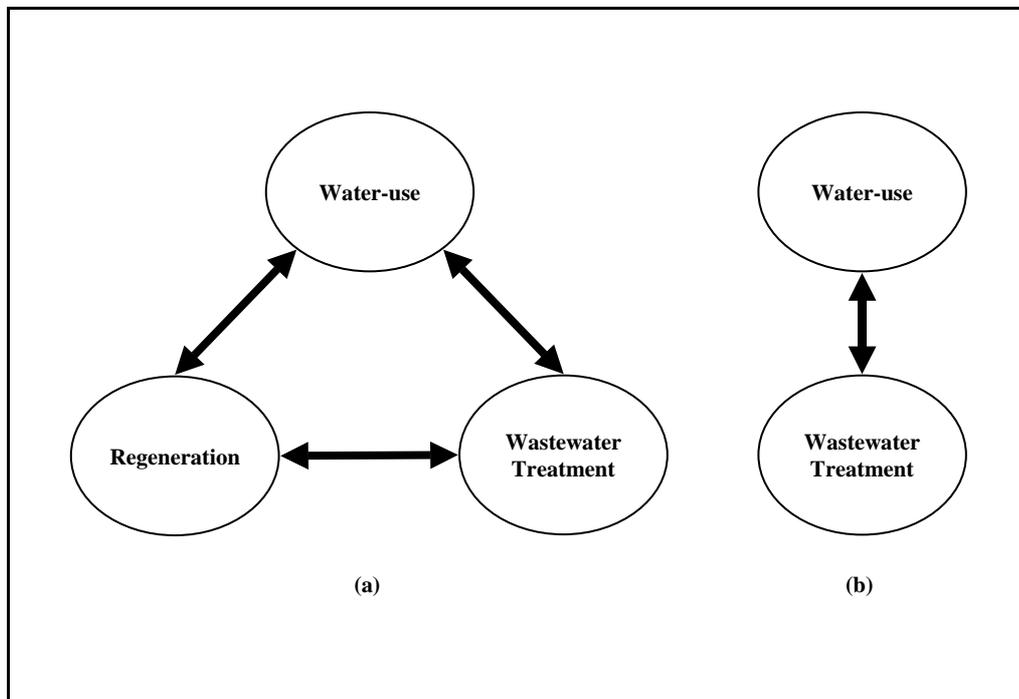
Figure 2.2. *Conceptual models of the water system in an industrial plant.*
(a) Three-subsystem conceptual model (Kuo and Smith, 1998a).
(b) Two-subsystem conceptual model.

Regardless of whether the water system is conceptualised as being composed of two subsystems or three, certain elements are common to both. Aside from water-using operations and wastewater treatment operations, water sources supply water to the process system and water sinks receive water from the process system. More generally, a water source is defined as the point at which a supply of water is available to the process system while a water sink is the point at which water is consumed by the process system (Linnhoff March Limited, 2001). Parthasarathy (2001) offers a generic definition of a source as being any stream in the process system which carries with it a species of interest. A sink is correspondingly any unit within the process system which is capable of handling the species of interest. Sources are subsequently categorised by Parthasarathy into fresh sources, which contain fresh species and are typically obtained externally, and process sources, which have been generated within the process system.

2.1.5 Design Approaches for Water Systems

In a recent review on the field of water-reuse networks, Bagajewicz (2000) identifies two approaches for the design of water-use networks, namely conceptual approaches and mathematical programming. Conceptual approaches include primarily the Pinch Analysis based graphical targeting and design methods in which system targets, for example, the freshwater flowrate target, are set ahead of the design stage. The advantage of these methods is that they provide valuable conceptual insight into the performance or behaviour of the system under consideration. The approach has however shown limitations when dealing with complex systems. Mathematical programming sees the targeting and design stages being performed simultaneously. Being a computer based tool, the problem under consideration can be of a more complex nature. However, much of the conceptual insight available through the Pinch Analysis based approach is lost.

Ponton (1999) makes a general comment on all computer tools that while they provide answers that may be correct or appropriate, they fail to give an explanation or provide understanding of why a particular solution is good. As such, Ponton criticises the fact that optimisation packages provide a single answer and claim it to be the best solution, since this provides no information on the relative superiority of the solution and is dependent on the specific criteria for what is considered *best*. Recent approaches to the design of water-use systems see a combination of the two approaches with the insight from the conceptual Pinch Analysis based approaches being incorporated into the formulation of mathematical programming models (Bagajewicz, 2000). Bagajewicz comments that the field has developed from one in which conceptual insight was used to obtain a design to one in which mathematical programming is used to produce a design with a graphical representation of the system being obtained from this solution.

A third approach to the design of water-use systems, distinct from the conceptual and mathematical programming approaches, has emerged in heuristic/algorithmic based approaches. The characteristic of these approaches is that they do not have a distinct targeting and design stage, nor do they rely on mathematical programming. Instead the design and the system target evolve simultaneously through the implementation of a systematic procedure. The use of the heuristic/algorithmic approach in combination with the mathematical programming approach has also found application.

2.1.6 Review Structure

This section has established a number of key concepts in the design of water systems around which the rest of the review will be structured. The different approaches will be considered separately and in the order of conceptual approaches, heuristic/algorithmic approaches and mathematical programming approaches. The conceptual approaches will be used to establish key ideas which have been transferred to the other approaches. Distinction will also be made regarding the method of analysis in terms of separate and simultaneous consideration of the

water-using and wastewater treatment subsystems. Finally differentiation between single contaminant and multiple contaminant approaches will be made. The remainder of the review begins with a brief review of the Mass-Exchange Network (MEN) Synthesis theory from which the conceptual approaches have developed.

2.2 MEN SYNTHESIS

The development of conceptual methods for water-use system design has been influenced by the theory from MEN Synthesis. **Section 2.2.1** examines the coinciding link between MEN Synthesis and water minimisation. A number of other concepts and ideas carried over from the field of mass-exchange networks to the field of water-use system design are presented in **Section 2.2.2**.

2.2.1 The Link between MEN Synthesis and Water Minimisation

The analogy between heat transfer and mass transfer mechanisms has long been recognised. El-Halwagi and Manousiouthakis (1989) recognised that there were similarities, but also differences, between the mass transfer of species from a set of species-rich streams to a set of species-lean streams, and the transfer of energy from a set of hot streams to a set of cold streams. These similarities suggested that a similar design method to that developed for heat-exchange networks (Linnhoff and Flower, 1978; Linnhoff and Hindmarsh, 1983) might be possible for the design of mass-exchange networks. The differences between heat transfer and mass transfer mechanisms however indicated that the design of mass-exchange networks involves a problem of higher dimensionality due to the differing criteria for thermal equilibrium and phase equilibrium.

Thermal equilibrium between a pair of hot and cold streams is established when the temperatures of both the hot stream and cold stream are the same and does not depend on the nature of either stream; only one conserved quantity is transferred, namely energy, and thus temperature represents the sole equilibrium criterion for the system. For mass-exchange, the distribution of species between two phases is determined by the phase equilibrium characteristics of the solute-solvent system. In addition, the number of conserved quantities which are exchanged in mass transfer can be large. Thus, in addition to the temperature of the different phases being the same, phase equilibrium is dependent on the nature of the solute-solvent system and the distribution of species between the phases.

MEN Synthesis is defined as *the systematic generation of a cost-effective network of mass-exchangers with the purpose of preferentially transferring certain species from a set of rich streams to a set of lean streams* (El-Halwagi and Manousiouthakis, 1989). The *mass-exchangers* that this definition refers to include almost any countercurrent, direct-contact mass transfer operation that uses a Mass-Separating Agent (MSA) for the selective transfer of certain solutes; for example, absorption, liquid-liquid extraction and ion-exchange, to name but

a few. MEN Synthesis thus has application in the chemical process industry in the areas of feed preparation, product separation, material recovery and pollution prevention. For pollution prevention, MEN Synthesis extends to the transfer of certain undesirable species from a set of rich streams (containing a high concentration of the undesirable species) to a set of lean streams or MSAs (containing a low concentration of the undesirable species). The problem, in its basic form, may be stated as follows (El-Halwagi, 1997):

Given a set of rich streams and a set of MSAs (lean streams), synthesise a system of cost-effective mass-exchangers that can preferentially transfer certain undesirable species from the rich streams to the MSAs. The flowrate of each rich stream and its supply and target composition are known, as are the supply and target composition of each MSA. The flowrate of each MSA is unknown and is to be determined so as to minimise the network operating cost. The set of MSAs comprises Process MSAs, which are already available on the plant site and can be used at very low cost, and External MSAs which have to be purchased. Minimising the operating cost for the network therefore extends to maximising the use of the Process MSAs and minimising the amount of External MSAs required to achieve the overall mass-exchange task. The flow of Process MSAs is however limited according to their availability on the plant.

El-Halwagi and Manousiouthakis (1989) solve this problem using a two-stage approach for a system in which separation targets can be set for a single component. The minimum amount of external MSA required to achieve the overall mass-exchange task is determined in the first stage (without there being any commitment to a particular design configuration) while the design featuring the minimum number of mass-exchangers required to achieve the targeted flow of external MSA is determined in the second stage. The method is directly analogous to that proposed by Linnhoff and co-workers for the design of heat-exchange networks (Linnhoff and Flower, 1978; Linnhoff and Hindmarsh, 1983).

Not all MEN Synthesis problems involve Process MSAs; in such cases only External MSAs are used to achieve the mass-exchange task. In the event of only one External MSA being used (whether in combination with Process MSAs or not) the task of synthesising a cost-optimal mass-exchange network degenerates into one of minimising the amount, and therefore the cost, of External MSA used to accomplish the mass-exchange task (El-Halwagi and Manousiouthakis, 1989). Water minimisation, in which water is used as the sole MSA associated with the removal of a certain contaminant species from a set of rich streams in a system of mass-exchange operations is thus an example of this kind of problem (Hallale and Fraser, 1998), and the starting point of the work on the design of optimal water-use systems by Wang and Smith (1994a).

Having reviewed the coinciding link between MEN Synthesis and water minimisation, the remainder of the field of MEN Synthesis is not reviewed here. A number of final concepts and ideas from MEN Synthesis are however noted. Reviews and overviews of the field of MEN Synthesis are provided by El-Halwagi (1997; 1999), El-Halwagi and Spriggs (1998), Spriggs and El-Halwagi (2000). An overview of capital cost targeting in MEN Synthesis is provided by Fraser and Hallale (2000) while Grossmann et al. (1999) provide an overview of the application of mathematical programming to MEN Synthesis.

2.2.2 Final Concepts and Ideas from MEN Synthesis

Analogous to the minimum temperature difference specified in heat-exchange network design, a minimum concentration difference is specified in MEN Synthesis. This concentration difference ensures that there is sufficient driving-force for mass transfer and represents a compromise between capital and operating costs. Where the pinch point in heat-exchange network design corresponds to that region of the heat-exchange network in which the minimum temperature driving-force for heat-exchange is reached, the pinch point in MEN Synthesis corresponds to that region of the mass-exchange network at which the minimum concentration driving force for mass-exchange is reached. Thermodynamically, it is thus the most constrained region of the system.

The problem considered by El-Halwagi and Manousiouthakis in their initial research involves once-through MSAs only (El-Halwagi and Manousiouthakis, 1989), for which there is neither an economic nor environmental incentive to force either the recovery of the transferred species or the regeneration and recycle of the MSA. For the case of regenerable MSAs however, strong economic and/or environmental incentives exist for the recovery of the transferred species and/or the regeneration of the MSA. El-Halwagi and Manousiouthakis (1990a) give consideration to this situation and propose a two-step procedure for the simultaneous synthesis of mass-exchange and regeneration networks involving a single (key) contaminant.

A further notable extension to the MEN Synthesis field sees the use of chemical MSAs, which have higher selectivities and capacities compared to physical-type MSAs, to achieve the required separation task (El-Halwagi and Srinivas, 1992; Srinivas and El-Halwagi, 1994a; Warren et al., 1995). The use of chemical MSAs which involves chemical reactions together with interphase mass transfer and the mass-exchange synthesis task is termed Reactive Mass-Exchange Network or REAMEN Synthesis.

The concept of Waste Interception and Allocation Network (WIN) Synthesis was introduced by El-Halwagi et al. (1996) as an extension of the MEN Synthesis concept. Instead of dealing with pollutant species at the terminal waste stream stage, the possibility of intercepting these pollutant-laden streams, through the introduction of mass-exchange operations, within the process system is considered. Apart from providing a single framework for dealing with both gaseous and liquid forms of pollution, the approach recognises that the pollutant load of a particular species in the gaseous phase is interrelated to that in the liquid phase. As such it may be easier to solve a pollution problem that exists in the liquid phase by intercepting a gaseous stream containing that pollutant before the transfer to the liquid stream takes place, and vice versa. Figure 2.3 contrasts the schematic representation of a waste interception and allocation network with that of a mass-exchange network (El-Halwagi et al., 1996). In addition to the basic objectives of MEN Synthesis, WIN Synthesis aims to identify which of the process streams, gaseous or liquid, should be intercepted, the extent to which the pollutant should be removed from these streams, and which of the candidate MSAs should be employed to accomplish the task.
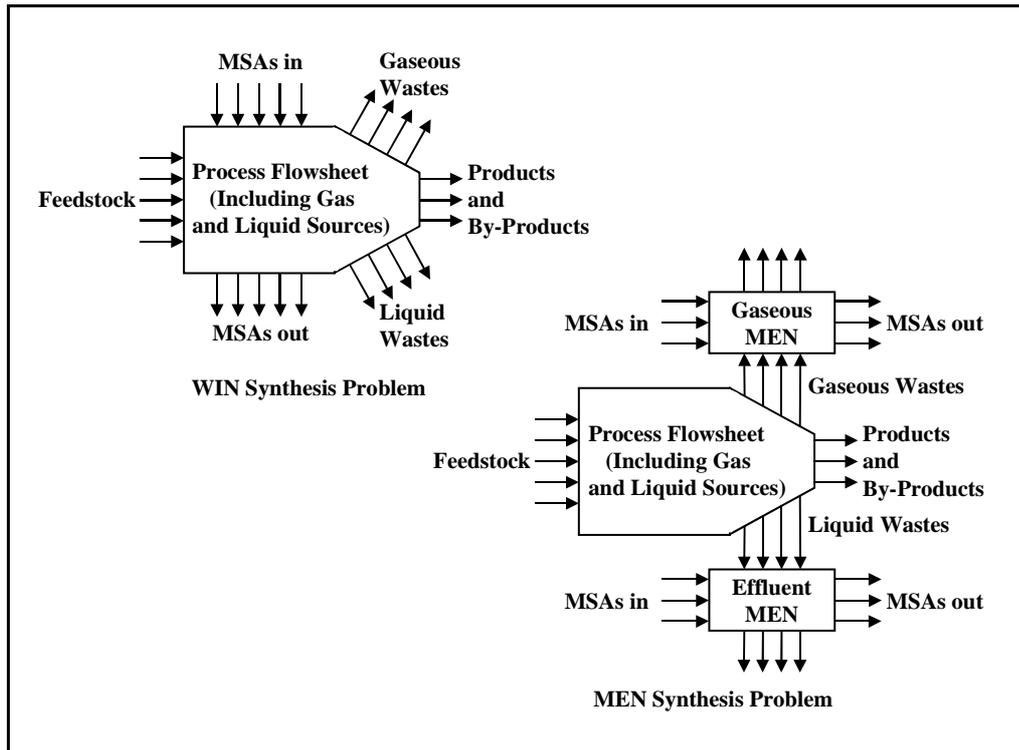
Figure 2.3. *Schematic diagram contrasting the WIN Synthesis and MEN Synthesis problems (El-Halwagi et al., 1996).*

2.3 CONCEPTUAL APPROACHES TO WATER SYSTEM DESIGN

Water system design via conceptual approaches involves two stages. During the first stage, a target is identified for the water system without any commitment to a particular network design configuration; the second stage involves the design of a network which achieves the predicted target. This section reviews the conceptual approaches to water system design. **Section 2.3.1** considers the water minimisation problem while **Section 2.3.2** considers the effluent treatment problem. Approaches which consider both the water minimisation and effluent treatment problems simultaneously are reviewed in **Section 2.3.3**.

2.3.1 Separate System Design - Water Minimisation

Wang and Smith (1994a) present a two-stage graphical approach to minimising the amount of water used by a process system comprising mass-exchange operations. An overriding assumption in this approach is the division of the process system into a set of so-called process streams and a set of water streams. The nature of the process streams is such that their flowrates, inlet and outlet contaminant concentrations are set by the process system. Given that the mass-load of contaminant transferred via mass-exchange from the process streams is equal to the mass-load of contaminant received by the water streams, only the water streams are considered in the analysis. The process streams are represented by fixed mass-loads of

contaminant transferred to the water streams together with contaminant concentration limits applied to the water streams, which take the place of the more rigorous mass-exchange equilibrium relationships that exist between the process streams and the water streams. Figure 2.4a shows a single mass-exchanger and the contaminant concentration profiles for the process stream and water stream. The corresponding representation of this mass-exchanger in Wang and Smith's approach is presented in Figure 2.4b.
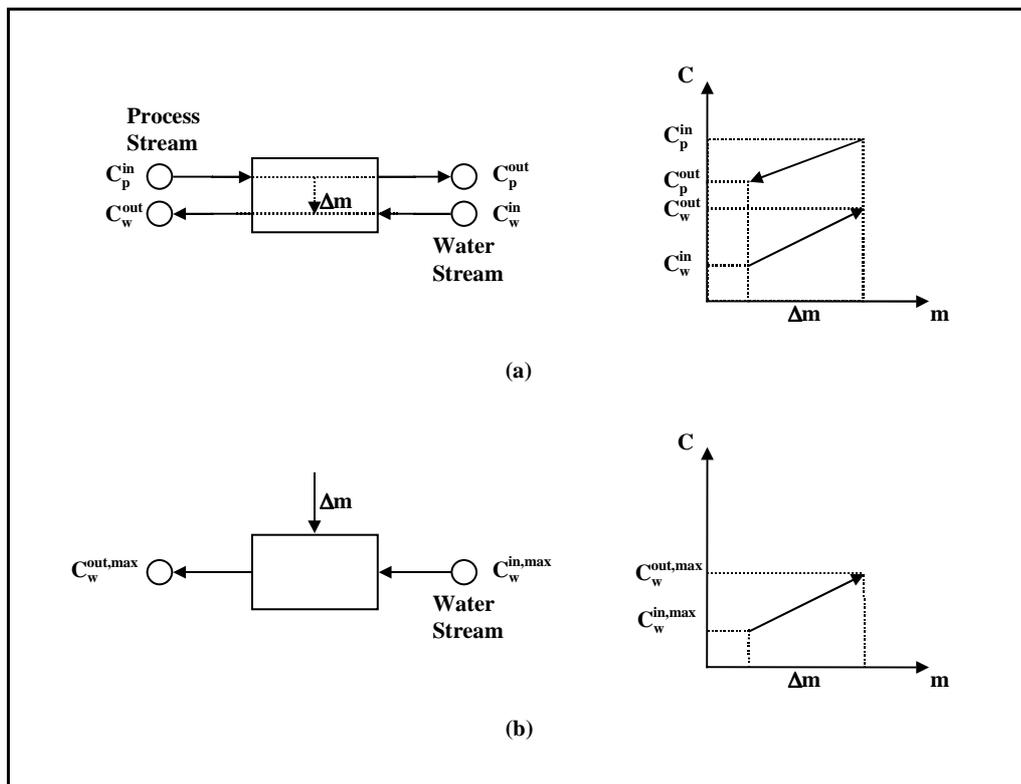
Figure 2.4. *The representation of a mass-exchanger in the conceptual approach of Wang and Smith (1994a). (a) A single mass-exchanger and the associated contaminant concentration profiles for the process stream and the water stream. (b) The representation of the same mass-exchanger in the approach of Wang and Smith with only the water profile of the operation considered explicitly.*

Thermodynamic feasibility is not the only reason for the imposition of contaminant constraints on the water stream. Other factors which necessitate the imposition of contaminant constraints include avoiding precipitation, fouling and corrosion amongst other effects (Wang and Smith, 1994a).

Mathematically, the relationship between the water flowrate through the operation and the inlet and outlet contaminant concentrations may be expressed by:

$$\Delta m = F_w (C_w^{out} - C_w^{in})$$

2.1

where Δm is the mass-load of contaminant transferred from the process stream to the water stream, F_w is the water flowrate (which is considered to be constant across the operation), and C_w^{in} and C_w^{out} are the contaminant concentrations at the inlet and outlet respectively.

Although the flowrate, inlet and outlet contaminant concentrations for the process stream are fixed, that is, the contaminant concentration profile for the process stream is fixed, there is a range of contaminant concentration profiles for the water stream that will achieve the required mass-exchange task (Figure 2.5a). As such there is a range of feasible flowrates and inlet and outlet contaminant concentrations for the water stream. At the limit of this range is the limiting water profile (Wang and Smith, 1994a) which represents the boundary between feasible and infeasible process operation. Water-reuse from other operations within the process system will be maximised if water enters an operation at the maximum inlet concentration that operation will tolerate. The limiting water profile for an operation then corresponds to the minimum amount of water required to achieve the mass-exchange task when water enters the operation at its maximum or limiting inlet concentration. This minimum flowrate further corresponds to the water leaving at its maximum or limiting outlet concentration. Feasible process operation will therefore be realised by any water supply line which lies at or below the limiting water profile as shown in Figure 2.5b.
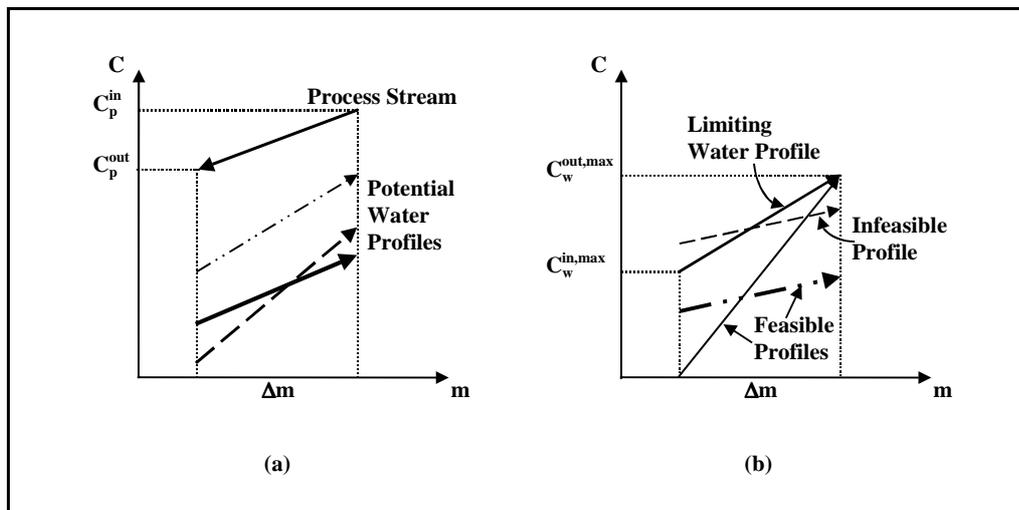
Figure 2.5. *Diagram illustrating the concept of the limiting water profile (Wang and Smith, 1994a). (a) Different water profiles with different water flowrates and contaminant concentrations may be able to satisfy the requirements of the process. (b) The limiting water profile alongside feasible and infeasible water profiles.*

The significance of the limiting water profile is that it allows a common basis for the analysis of a range of operations for which the concentration constraints arise due to different effects, for example, corrosion or mass transfer driving-force (Wang and Smith, 1994a). It is noted that it is inherently assumed by this approach that the functioning of the process operation is independent of the concentration of contaminants present in the water. The only requirements

are that the contaminant concentrations in the water entering and leaving the process operations are below or at the limiting values. This assumption is almost universally applied in all subsequent research in the field.

The targeting of the minimum water flowrate for a system of water-using mass-exchange operations involves the construction of a composite curve. Here the limiting water profiles of all the water-using operations are plotted on contaminant concentration versus contaminant mass-transferred axes. These profiles establish concentration intervals which coincide with the end points of the various limiting profiles. Figure 2.6a shows the limiting water profiles for four mass-exchange operations plotted on contaminant concentration versus contaminant mass transferred axes together with the concentration intervals established by these profiles. The construction of the limiting composite curve is completed by summing, within each concentration interval and across all limiting profiles, the mass-load of contaminant transferred within that interval, as shown in Figure 2.6b. The minimum amount of freshwater required by the system is determined by rotating a line about the contaminant concentration of the freshwater supply (Figure 2.6c) such that it becomes tangential to the limiting composite curve, as shown in Figure 2.6d. The inverse of the slope of this water supply line represents the minimum flowrate of water necessary to satisfy the mass transfer requirements of the system. The concentration at which the water supply line touches the composite curve is termed the pinch point.
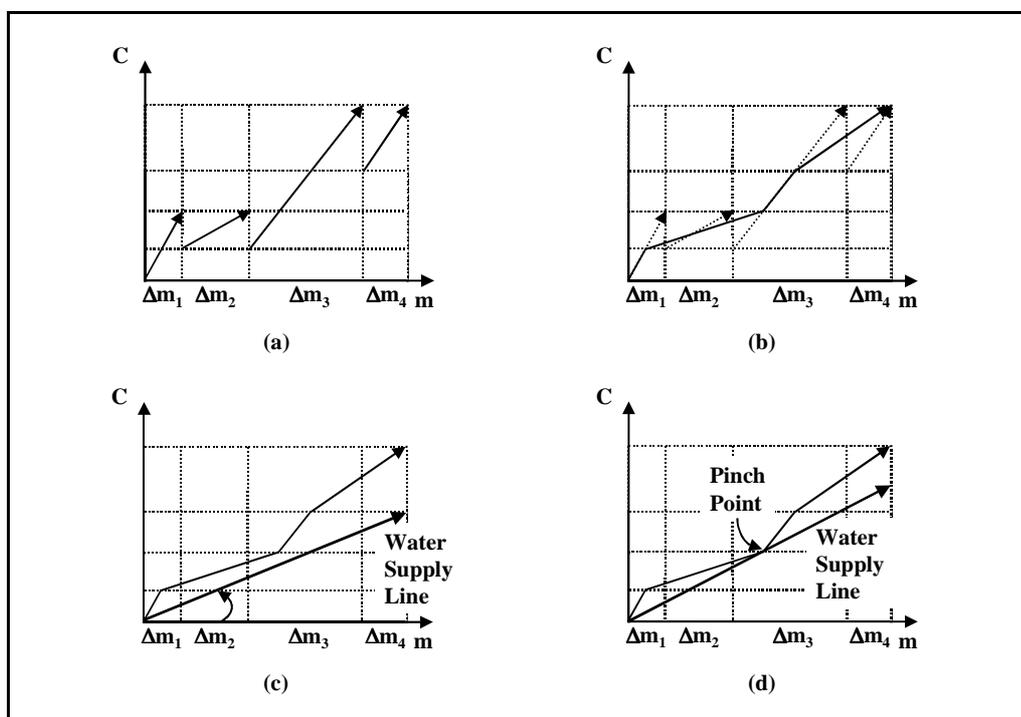
Figure 2.6. *Graphical targeting of the minimum water flowrate for a system of mass-exchange operations (Wang and Smith, 1994a). (a) Placement of the limiting water profiles for the individual operations. (b) Construction of the limiting composite curve. (c) Rotation of the water supply line about the water supply concentration. (d) Minimum water flowrate water supply line with pinch point.*

Pinch points arise at each point of contact between the water supply line and the limiting composite curve. This point of contact represents a region in the system where a further reduction in the water consumption by the system is not possible due to some contaminant concentration limit having been reached.

Wang and Smith (1994a) propose two strategies for obtaining designs which achieve the predicted target, namely the maximum driving-force method and the minimum number of water sources method. These methods involve the design of an initial flow network based on information obtained from the targeting stage. This network is evolved, through the breaking of loops in the network, to remove unnecessary network complexity. It should be noted that the minimum number of water sources refers to the number of sources feeding a particular operation; the system as it is considered in the initial exposition of the approach has only a single freshwater source. The water flow network derived from the minimum number of water sources method for the example presented in Figure 2.6 is presented in Figure 2.7.
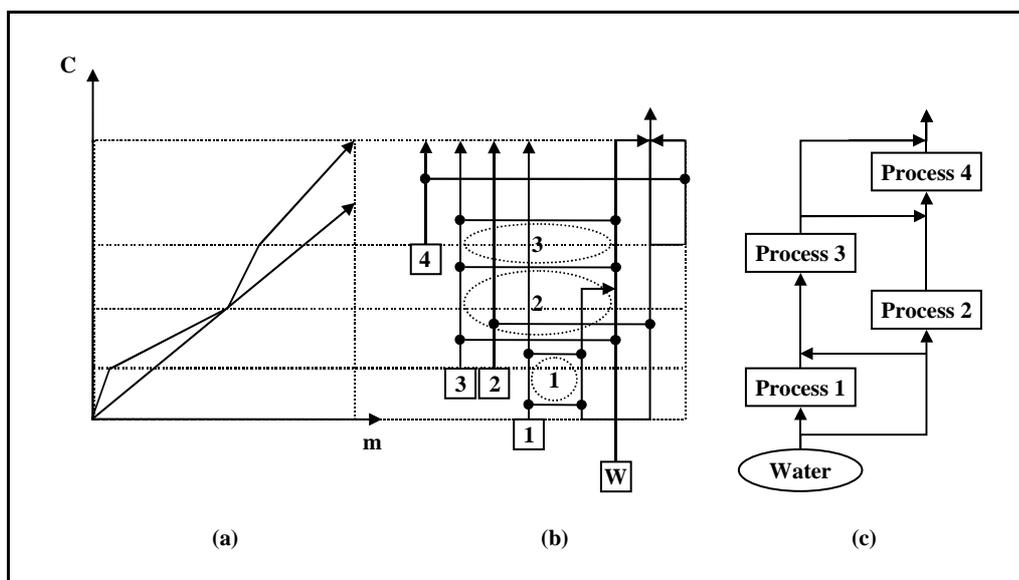
Figure 2.7. *The minimum water sources design method for obtaining a design which achieves the predicted target (Wang and Smith, 1994a). (a) Limiting composite curve with water supply line. (b) Grid diagram showing the water-use network with loops. (c) Final network following network evolution through loop breaking.*

Wang and Smith (1994a) extend the graphical targeting methodology to systems involving multiple contaminants. Here, the multiple contaminant nature of the problem is incorporated into the analysis by adjusting the limiting water profiles for the various operations such that at each concentration interval boundary, at least one of the contaminants is at its limiting concentration. The procedure begins with the selection of a reference contaminant and a reference process. Making the assumption that the mass-exchange of one contaminant is linearly related to that of another, all of the other processes and contaminants are shifted

relative to these references. As was the case for the single contaminant situation, the limiting composite curve is formed from the limiting water profiles of the individual operations and the placement of the water supply line proceeds as previously. The approach for multiple contaminants is systematised by an algorithmic procedure (Wang and Smith, 1994a). While the assumption is made that at least one contaminant is at its limiting concentration at each concentration interval boundary, others are not necessarily at their limits. This key concept is formalised by Alva-Argáez (1999) who introduces the definitions of limiting and non-limiting contaminants. As such, limiting contaminants refer to those contaminants which reach their maximum limits and determine the water demand for the operation. Non-limiting contaminants emerge from the operation at a concentration below their maximum limits and do not affect the water demand for that operation.

Having identified the minimum freshwater flowrate in the targeting procedure, the possibility of reducing the amount of freshwater needed by the process system via the introduction of a regeneration process is considered by Wang and Smith (1994a). The introduction of the regeneration process allows some of the effluent, which would otherwise have been prevented from being used, to be reused within the process system. In this way, freshwater-use is reduced beyond the level of water-reuse alone. Accompanying the regeneration process is a cost associated with regeneration. Hence, in addition to determining the minimum freshwater flow required by the process system, the minimum flowrate of water to be regenerated must be determined. The targeting and design procedure is thus extended to include regeneration processes and two cases are considered, namely regeneration reuse and regeneration recycling. The placement of the regeneration process is shown to be optimal if it accepts water at the pinch concentration; this water is then regenerated to a quality below the pinch concentration. Regeneration processes with fixed outlet concentrations and mass-load removal ratios are considered. Figure 2.8 illustrates the inclusion of a regeneration process in the graphical targeting method. It is noted that from Figure 2.8a it appears that the water supply line crosses the limiting composite curve thereby reflecting an infeasible operating situation. However, by creating a composite of the water supply lines as shown in Figure 2.8b, feasibility is re-established.

Various shortcomings or oversights of this initial theory on regeneration targeting have been reported and further work carried out by Castro et al. (1999) and Mann and Liu (1999).

The use of multiple freshwater sources of different qualities is considered in an extension to the basic methodology presented by Wang and Smith (1995a). The assumption is made that there is an infinite amount of the different water sources available and that the cost of the water increases with improving water quality. With a single freshwater source available, targeting the minimum freshwater flowrate minimises the water cost simultaneously. However, when multiple water sources are involved, targeting aims to minimise the overall water cost. As a result, the water supply line is matched against the limiting composite curve such that the use of high cost water (high quality) is minimised. Figure 2.9a illustrates the composite curve and water supply line for the case where three different freshwater sources of different qualities are available and for which the costs are proportional to improving quality.
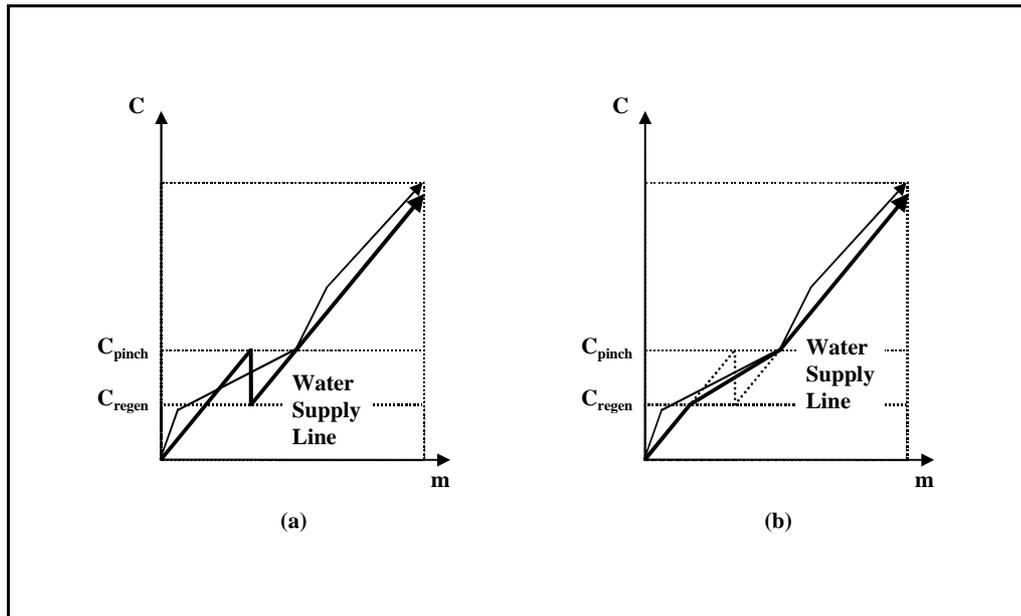
Figure 2.8. *The incorporation of a regeneration operation into the graphical targeting procedure (Wang and Smith, 1994a). (a) Regeneration of water at the pinch concentration. The water supply line appears to cross the limiting composite curve reflecting an infeasible operating situation. (b) The composite water supply line resolves the apparent feasibility violation.*
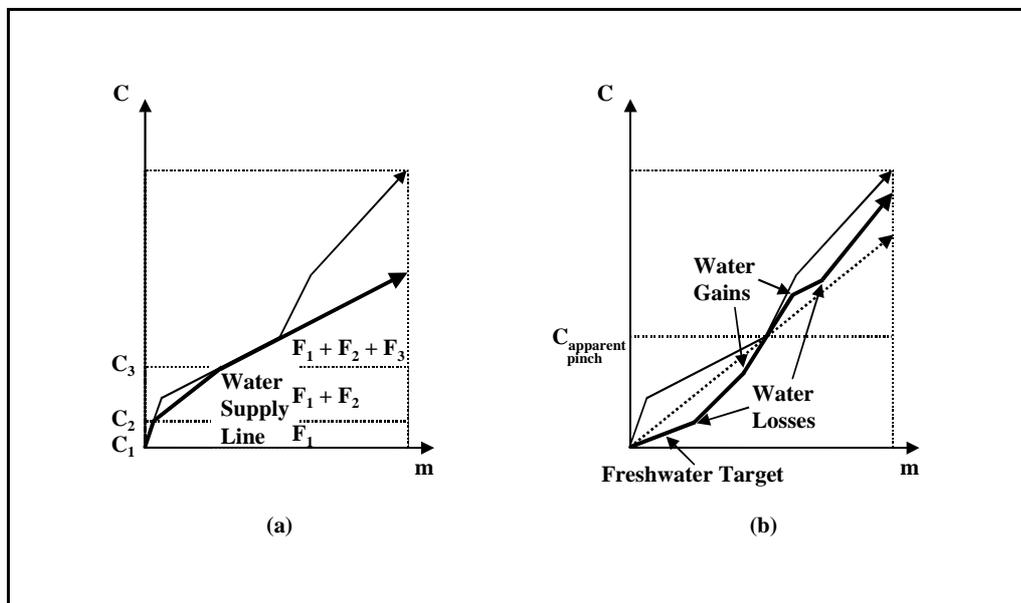
Figure 2.9. *Two extensions to the basic graphical targeting approach. (a) Graphical targeting for a system with three freshwater sources of varying quality. There are no availability constraints on these sources; the costs of the sources vary with quality with F_1 being most expensive and F_3 being least expensive (Wang and Smith, 1995a). (b) The effect of water losses and gains in the prediction of the minimum freshwater target.*

The incorporation of finite water sources, that is, water sources for which there is a fixed availability into the graphical targeting procedure is indirectly presented by Wang and Smith in their consideration of operations with finite water losses and water gains (Wang and Smith, 1995a). For these operations, the assumption is made that water losses occur at the limiting inlet concentration and water gains occur at the limiting outlet concentration. The targeting procedure for determining the minimum water requirement for the system involves targeting the minimum water flow for the system without water losses and gains. Losses and gains are subsequently incorporated into the water supply line. Mann and Liu (1999), who give further consideration to this problem, comment that the pinch point determined without consideration of the losses and gains is an apparent pinch point since it may change once the flowrate losses and gains are incorporated into the targeting procedure. According to Mann and Liu (1999), water losses below the so-called apparent freshwater pinch concentration will generally result in an increase in the overall freshwater requirement for the system and correspondingly a decrease for water gains. As such, the change in the freshwater consumption of the system depends on the level of contamination present in the water lost or gained. Above the apparent freshwater pinch, a water gain has no effect on the overall freshwater target for the system, however a water loss may or may not increase the freshwater target. If the loss of water above the apparent freshwater pinch concentration is sufficiently large, an increase in the overall freshwater target and a change in the location of the pinch concentration will occur. Figure 2.9b illustrates the effects of finite water gains and water losses on the water supply line and the prediction of the minimum freshwater target for the system.

The work on the incorporation of water losses and gains into the targeting procedure is subsequently pursued by Savulescu (1999) who highlights shortcomings in the method of Wang and Smith related to the accurate prediction of the freshwater target. It should be noted that for systems in which flowrate changes occur, the volume of freshwater used by the process system is different from the volume of wastewater produced (Mann and Liu, 1999).

A key assumption made by Wang and Smith in their approach is that the process operation's functioning is not affected by changes in the flowrate of water used to accomplish the mass-exchange task. The incorporation of fixed flow operations into the analysis is subsequently considered (Wang and Smith, 1995a). Here it is demonstrated that the established targeting approach remains applicable and that the amount of water required by the fixed flow operations can be achieved by local recycling (around the operation) or, in cases where this is not allowed, splitting the operation in such a way that water from one part of the process operation is used in the next part. Savulescu (1999) extends the work of Wang and Smith on minimum water flowrate targeting for fixed flow operations for which local recycling and operation splitting are not allowed.

With many operations not permitting a wide range of flowrates and others not falling into the mass-exchange category, a different graphical targeting approach, called the Two-Composite Plot, is introduced by Buehner and Rossiter (1996) and Dhole et al. (1996). With this approach, each water-using operation is conceptualised as being made up of inlet streams (water demands) and outlet streams (water sources) and the possibility does exist that there are

several of each of these, and that each may have a different water quality associated with it. All of the input streams are plotted on axes of purity versus water flowrate and combined to form the Demand Composite. Similarly, the outlet streams are plotted and combined to form the Source Composite. In determining the minimum freshwater flowrate required by the system, the Demand Composite is shifted horizontally such that it just makes contact but does not cross the Source Composite; the point of contact between the two composites is termed the pinch point.

The overlap between the Source Composite and Demand Composite defines a region of water-reuse, the further expansion of which is limited by the pinch point. To the right of this region, the demand for high purity water exceeds the available supply and the deficit is made up using freshwater. To the left of this reuse region, the water sources constitute the wastewater produced by the system owing to there either being insufficient demand for this water or a restriction on the reuse of this water due to its associated quality. Mann and Liu (1999) suggest slightly different definitions of the pinch point for the Two-Composite Plot (termed the Water-Source and -Demand Plot by these authors). According to these authors, the freshwater pinch, which corresponds to a vertical line on the (relative) flowrate axis, designates the boundary between the region of water-reuse and that of freshwater make-up while the reuse pinch identifies the boundary between the water-reuse region and that of wastewater production. Figure 2.10 shows an example of the Two-Composite Plot with the pinch point along with the various regions of the plot indicated. It should be noted that the numbers on the purity axis decrease since purity is measured according to the level of contamination present in the water source; freshwater, which corresponds to absolute purity, thus occupies the highest point on the axis.

In achieving a network design which achieves the targeted freshwater flowrate, Dhole et al. (1996) note that sources should provide water to demands on the same side of the pinch point. The use of a water source above the pinch to satisfy a water demand situated below the pinch will result in the freshwater target being exceeded. The use of freshwater below the pinch produces a similar effect.

One attribute common to both the Wang and Smith approach and its extensions and the Two-Composite methodology is that it identifies those regions of the system which have the greatest impact on the overall water consumption by the system (or the cost associated with water-use in the system) (Wang and Smith, 1995a; Buehner and Rossiter, 1996; Dhole et al., 1996; Mann and Liu, 1999; Polley and Polley, 2000). More generally, the provision of this global insight is a common attribute of all Pinch Analysis based approaches (Linnhoff, 1993; Linnhoff et al., 1994; Buehner and Rossiter, 1996).

One approach to increasing the level of reuse within the system involves the mixing of water sources located adjacent to the pinch point (Buehner and Rossiter, 1996; Dhole et al., 1996). This results in the formation of a water source of intermediate quality, but of suitable quality to satisfy the demand currently creating the pinch. Water-reuse is increased and correspondingly freshwater-use and wastewater production decreased. Figure 2.11a illustrates these effects. Polley and Polley (2000) propose that this mixing strategy be such that it maximises the uptake

of contaminant by the water demand. By mixing the water sources such that the contaminant concentration is just sufficiently less than the demand's limiting concentration, the overall use of freshwater by the system will be minimised at the same time.
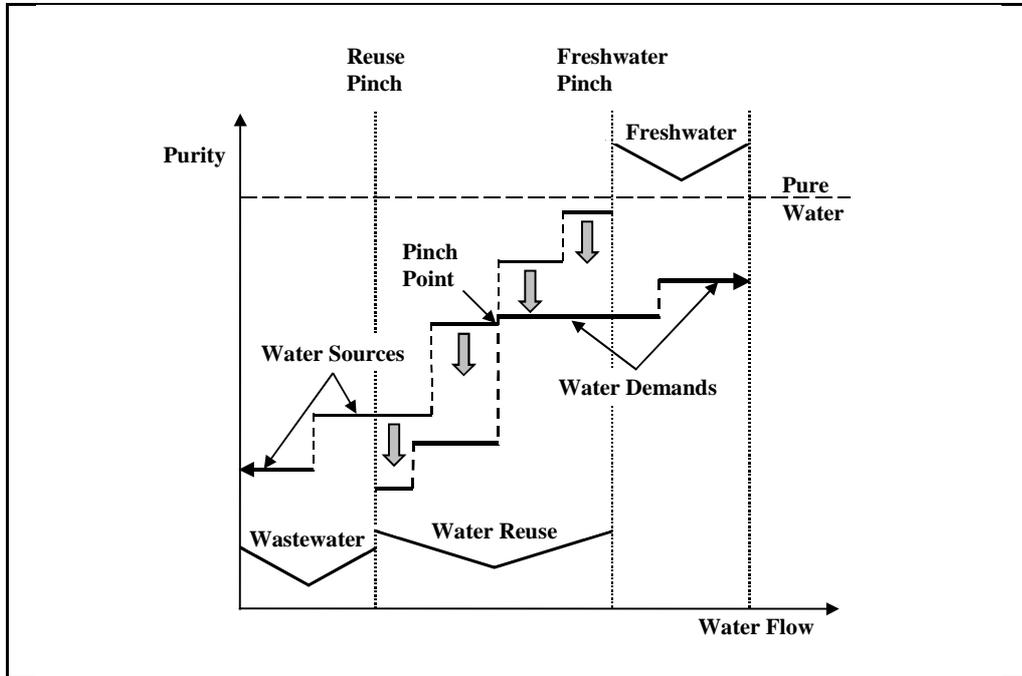
Figure 2.10. *The Two-Composite Plot for minimum freshwater flow targeting with the pinch point and regions of water-reuse, freshwater-use and wastewater production indicated (Buehner and Rossiter, 1996; Dhole et al., 1996; Mann and Liu, 1999).*
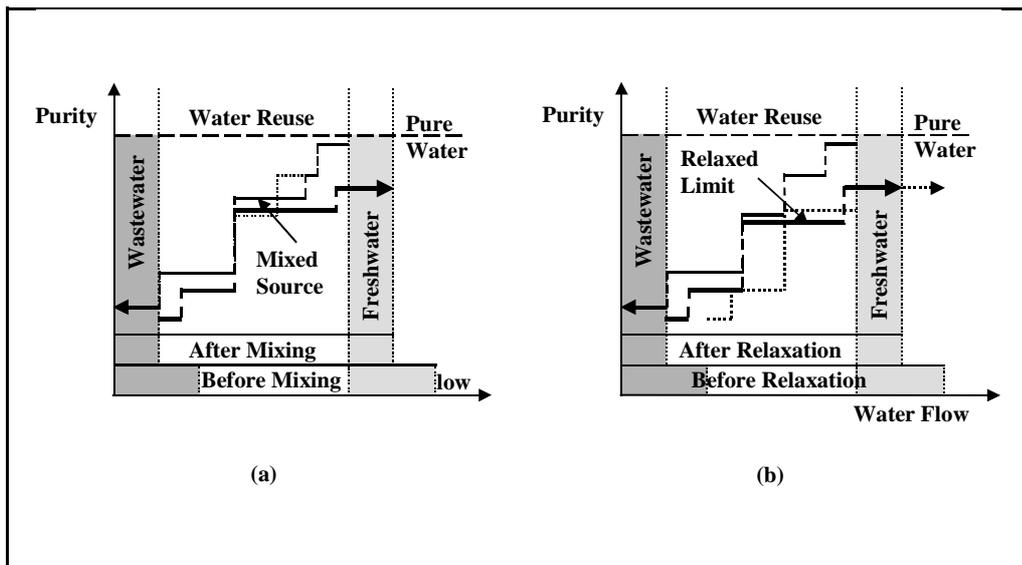
Figure 2.11. *Graphical representation of the effects of process changes on the freshwater target. (a) The effect of mixing sources adjacent to the pinch point. (b) The effect of relaxing the concentration limit on the demand adjacent to the pinch point.*

In addition to mixing water sources on either side of the pinch point, Mann and Liu (1999) propose the relaxation of the inlet concentration limit directly adjacent to the pinch point as a route to increasing the level of reuse within the process system. By effecting a process technology change to the demand currently creating the pinch, that is, a change which allows the demand to accept water of a lower purity, the level of water-reuse in the system is increased. This effect is illustrated in Figure 2.11b.

A more general philosophy to guide process changes which bring about a reduction in the freshwater flowrate target is the so-called Plus-Minus Principle, initially conceived to guide process changes in heat integration (Linnhoff and Vredeveld, 1984) and extended by Mann and Liu (1999) to water systems. The discussion presented by these authors is based on effecting process changes to a system of water-using mass-exchange operations for which the freshwater target is predicted via the approach of Wang and Smith (1994a). As a general principle, an increase in the limiting inlet and outlet concentrations of an operation will result in an increase in the concentration driving-force for mass transfer of the contaminant; this corresponds to a lower area requirement for mass-exchange and thus a lower capital expenditure. Process changes that are effective in reducing the freshwater requirement of the system should begin in the region below the freshwater pinch and should aim to shift the pinch concentration to a higher value. In targeting process changes for operations that exist across or directly below the freshwater pinch, increasing the maximum inlet or outlet concentrations will either reduce the mass-load of contaminant to be removed below the freshwater pinch, shifting the difference across the pinch concentration, or increase the freshwater pinch concentration. Both situations result in a reduction in the system's freshwater requirement.

In motivating the use of the Two-Composite methodology as opposed to the Wang and Smith approach, Polley and Polley (2000) characterise water demands as being either quality or quantity controlled. For quantity controlled operations, the amount of water is fixed regardless of the contaminant concentration whereas quality controlled operations have a varying water demand which depends on the level of contamination present in the influent water. As such, water-use systems may be characterised as being comprised of only quantity controlled operations, quality controlled operations, or both. The Two-Composite methodology is deemed suitable for systems which consist only of quantity controlled operations. This view is consistent with that of Mann and Liu (1999) who regard the approach as being suited to freshwater targeting for systems with fixed flow operations. The use of the approach to assess the retrofit potential of an existing water network is also noted (Mann and Liu, 1999).

In concluding this subsection on the conceptual approaches for the design of water-using systems, mention should be made of some of the other targeting and design approaches presented in the literature. These methods include: the targeting approach of Kuo and Smith (1998b); the Mass Problem Table of Castro et al. (1999), also termed the Concentration Interval Diagram by Mann and Liu (1999), the Water Sources Diagram reported by Castro et al. (1999); the Evolutionary Table, Design Table and Cascade Technique of Sorin and Bédard (1999a,b; 2000); and, the approach based on the Water Surplus Diagram reported by Hallale (2000; 2002). Other design procedures include those proposed by Oleson and Polley (1997),

the Water Mains Concept of Kuo and Smith (1998a) and the Mass Content Diagram reported by Mann and Liu (1999). Conceptual targeting methods for batch processes are proposed by Wang and Smith (1995b) and applied and extended by Majozi (1999).

As a final point to this subsection, Oleson and Polley (1996) give consideration to the conceptual targeting and design of systems involving geographical distance constraints. Here, the overall site is divided into different zones. Freshwater targeting is performed on the overall system and each of the individual zones and the pinch concentrations compared. Should the pinch concentration for a particular zone differ from that for the overall system, additional freshwater savings could be effected to that particular zone through the exchange of water between different zones.

2.3.2 Separate System Design - Wastewater Treatment

Having minimised the volume of freshwater used, and thus the amount of wastewater produced by the process system, attention becomes focussed on designing a network which will achieve the required level of treatment for the generated wastewater as economically as possible. The scope of this task extends to determining the optimal flow arrangement of wastewater streams between the different treatment operations; it does not however involve the screening of wastewater technologies and guidance on this issue is presented by Zinkus et al. (1998). The performance characteristics of the treatment operations are therefore known prior to the design being carried out. Two basic treatment models are considered, namely the fixed outlet concentration model and the mass-load removal ratio model (Wang and Smith, 1994b). The fixed outlet concentration model produces a treated effluent with a fixed outlet concentration regardless of the concentration of wastewater entering the operation. The quality of the treated effluent produced by the mass-load removal ratio model varies according to the mass-load of contaminant carried by the wastewater entering the operation. Figure 2.12a shows the basic process model for effluent treatment. The concentration profiles for a range of inlet concentrations are shown for both the fixed outlet concentration model and the mass-load removal ratio model in Figure 2.12b and Figure 2.12c respectively.

A two-stage conceptual design procedure, based on the targeting and design procedure for water minimisation, is presented by Wang and Smith (1994b) for the design of distributed effluent treatment systems. Based on the environmental discharge contaminant concentration limit, the mass-load of contaminant to be removed from each wastewater stream is determined and plotted on the concentration versus mass-load removed axes. Figure 2.13a shows the contaminant mass-load removal requirements for a system comprising four wastewater streams. The wastewater composite curve is constructed by summing the mass-load of contaminant to be removed from all of the wastewater streams in each concentration interval, as illustrated in Figure 2.13b. These concentration intervals are defined by the environmental discharge limit and the contaminant supply concentrations of the various wastewater streams. For the case where the treatment cost decreases continuously with decreasing flowrate, the minimum flow of wastewater requiring treatment is determined by rotating the treatment line about a specific point such that it just touches the wastewater composite curve as shown in Figure 2.13c. The

inverse of the slope of this treatment line represents the minimum flow of wastewater requiring treatment for the discharge concentration limit to be achieved. The specific location of the point about which the treatment line is rotated is determined by the nature of the treatment operation in terms of whether it may be characterised by a fixed outlet concentration or a mass-load removal ratio. Figure 2.13c shows the treatment line for an operation with a fixed outlet concentration while Figure 2.13d shows the treatment line for an operation with a mass-load removal ratio. The point at which the wastewater composite curve and the treatment line meet is called the treatment pinch concentration.
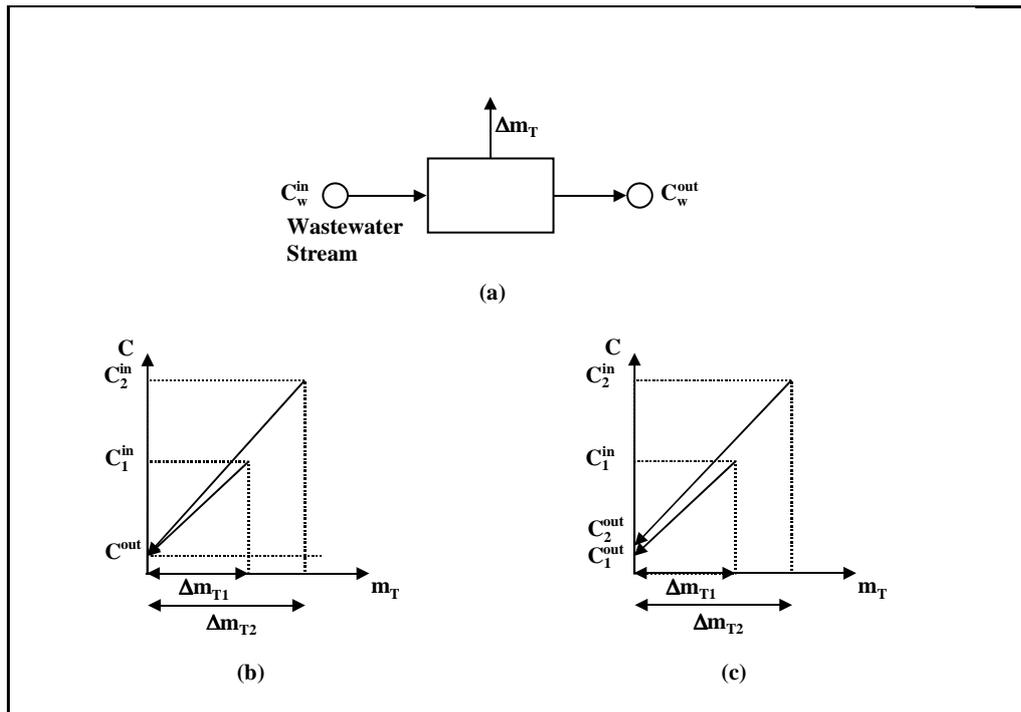
Figure 2.12. *The basic treatment model and the contaminant concentration profiles associated with different treatment models (Wang and Smith, 1994b). (a) The conceptual model for a water treatment operation. (b) The concentration profile of a treatment operations characterised by a fixed outlet concentration. (c) The concentration profile of a treatment operation characterised by a mass-load removal ratio.*

In designing a network which achieves the targeted treatment flowrate, the wastewater streams are classified into three groups according to whether their supply concentrations are below the pinch concentration, above the pinch concentration or at the pinch concentration. Those wastewater streams with concentrations above the pinch concentration are fully treated while those with concentrations below the pinch concentration bypass treatment. Wastewater streams at the pinch concentration are partially treated with some of the wastewater from these sources bypassing the treatment operation; the amount requiring treatment is determined via mass-balance. In their discussion on the significance of the treatment pinch concentration, Wang and Smith (1994b) note that it simply divides the system into two halves in terms of whether the wastewater is treated or not. The argument is presented that the wastewater

composite curve represents the mass-balance for the wastewater streams requiring treatment while the treatment line represents the mass-balance for the treatment operations.
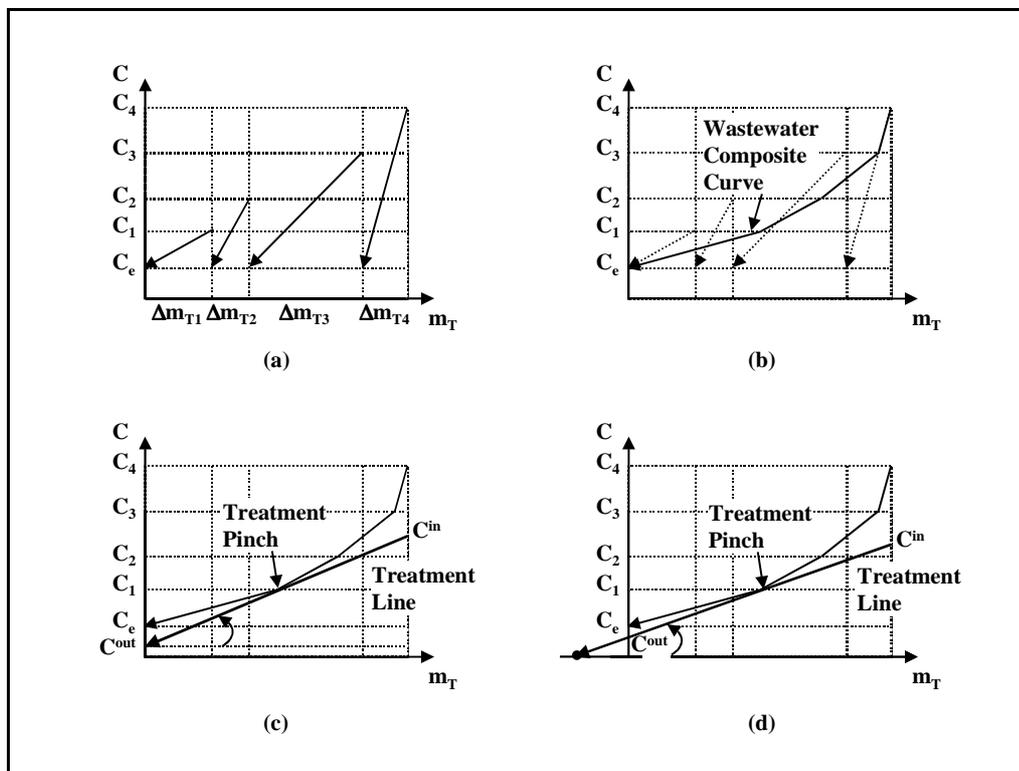
Figure 2.13. *Graphical targeting for distributed effluent treatment system design for a system of four wastewater streams (Wang and Smith, 1994b). (a) Placement of the individual wastewater streams on concentration versus mass-load axes (b) Construction of the wastewater composite curve. (c) Rotation of the treatment line for a treatment operation with a fixed outlet concentration. (d) Rotation of the treatment line for a treatment operation with a contaminant mass-load removal ratio.*

In one extension to the approach, treatment operations with maximum inlet concentration limits are considered. In addition, the approach is extended to deal with multiple treatment operations and wastewater streams involving multiple contaminants. For multiple treatment operations, the operation sequence is determined either by concentration constraints or economic considerations. Multiple contaminants are dealt with by considering the treatment requirements for each of the individual contaminants in turn and then taking the maximum treatment flowrate over all the contaminants.

The approach for the targeting and design of distributed effluent treatment systems is re-examined and developed by Kuo and Smith (1997). It is noted that for situations in which multiple treatment operations are required, the approach presented by Wang and Smith produces designs which are serial in nature, with the outlet of one treatment operation feeding the inlet of another. The composite treatment line, formed by combining the treatment lines of

the individual operations, is introduced to overcome this limitation. With this construction it is possible to identify those designs which feature the parallel operation of treatment operations.

In reviewing the approach proposed by Wang and Smith (1994b) for the design of distributed effluent treatment systems involving multiple contaminants, Kuo and Smith (1997) note that the approach does not always produce a feasible network design. In particular, the practice of combining all the designs based on single contaminant targeting to account for multiple contaminants fails to produce a feasible design if there exists a conflict between the aims for the removal of the different contaminants. Single contaminant targeting provides information as to how the wastewater streams should be segregated from the perspective of removing that particular contaminant. It does not however take into account how the wastewater streams should be segregated from the perspective of the other contaminants. The design based on single contaminant targeting is therefore likely to feature some degree of stream mixing, termed wastewater degradation, which is inappropriate from the perspective of other contaminants. The use of mixing exergy loss is proposed as a means of determining the optimal design for multiple contaminant treatment problems. This is done by minimising the mixing exergy loss over all contaminants in the positioning of treatment operations.

2.3.3 Simultaneous Systems Design

Kuo and Smith (1998a,b) motivate the use of an approach which considers the water-use, regeneration and effluent treatment subsystems simultaneously since it provides insight into the effect of design decisions, made for one subsystem, on the other subsystems. While wastewater minimisation through reuse and regeneration does result in a decrease in the volume of wastewater, the mass-load of contaminant present in the wastewater remains the same; as a result, the wastewater produced by the system is more concentrated. Depending on the extent of this increase in concentration, additional treatment units may be required in the effluent treatment system such that the required discharge concentration is achieved. The number of treatment operations required may be predicted in advance of designing the effluent treatment system by calculating the greatest effluent concentration that could be accepted by the operation based on the discharge limit and the performance of the treatment operation. Mathematically, this is given by:

$$C_{1,B} = \frac{C_e}{1 - RR_1} \qquad\qquad 2.2$$

where $C_{1,B}$ is the upper concentration boundary for the first treatment operation, RR_1 is the contaminant removal ratio which characterises the treatment operation and C_e is the environmental discharge concentration limit. If more treatment units are required, C_e is replaced in the formula by the upper concentration limit of the previous treatment operation. These concentration boundaries are plotted on the composite curve as shown in Figure 2.14a and identify the minimum number of treatment units required to treat the effluent. An assessment of the freshwater penalty required to reduce the number of treatment units is therefore possible.
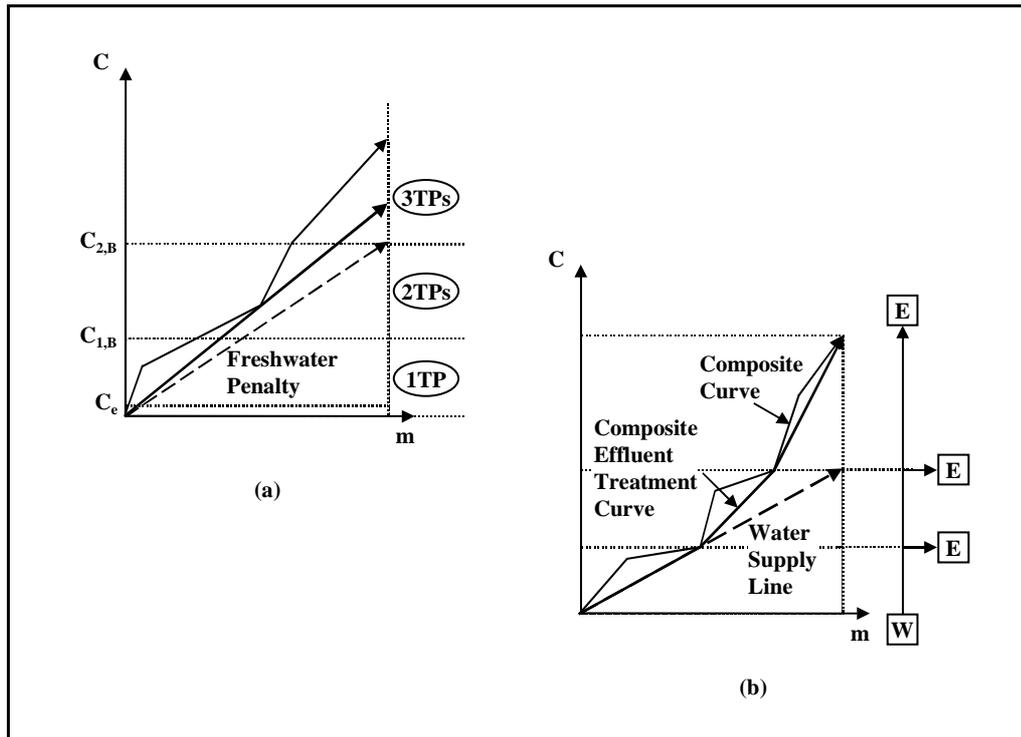
Figure 2.14. *Targeting methods for simultaneous systems design. (a) Prediction of the minimum number of treatment units required to treat the generated wastewater, with the freshwater penalty for reducing the number of treatment units indicated (Kuo and Smith, 1998b). (b) The sealing off of pockets on the composite curve provides information for the design of the effluent treatment system (Kuo and Smith, 1998a).*

In their targeting approach for water minimisation through reuse and regeneration Kuo and Smith (1998b) target the minimum freshwater-use and minimum regeneration flowrate as separate problems. If an increase in the freshwater flowrate is not considered a viable option in terms of reducing the number of treatment operations, it is proposed that some of the mass-load to be removed via effluent treatment be shifted to the regeneration system.

Kuo and Smith (1998a) introduce the Water Mains Concept as a simpler way of producing a network design which achieves the predicted flowrate target. This approach requires the sealing off of pockets on the limiting composite curve. The curve created by the sealing off of pockets is termed the lowest cost composite effluent treatment curve (Figure 2.14b). At each change of slope on this curve, a particular amount of water becomes available to the system; a portion of this water is reused while the rest is sent to effluent. The sealing off of pockets on the composite curve thus provides information about the nature of the wastewater streams generated by the system prior to the design of the water-use system being carried out. It is therefore possible to design the wastewater treatment system in advance of the water-use system. The impact of decisions made in the design of the water-use system on the wastewater treatment system can thus be quantified at an early stage of the design procedure.

2.4 HEURISTIC AND ALGORITHMIC APPROACHES TO WATER SYSTEM DESIGN

This class of approaches for the design of water systems has emerged primarily due to limitations encountered in applying the conceptual approaches to real systems, particularly in the area of multiple contaminant problems, and issues surrounding the optimality of solutions provided by mathematical programming approaches.

Liu (1999) defines *heuristics* as a set of rules based on engineering knowledge and experience which are widely used in chemical process design. These rules are a way of simplifying a complicated problem by using insight gained from a fundamental understanding of the problem (O'Young and Natori, 1999). According to the Oxford Dictionary, algorithmic approaches typically comprise a set of steps or rules for calculating a solution to a problem (Allen, 1991). The characteristic that sets these approaches apart from both conceptual design methods and mathematical programming approaches is that the system target and the design evolve simultaneously as the set of rules or steps is applied. It is noted that heuristic approaches which adopt an *ad hoc* attitude towards water minimisation, which further tend to be system specific, are not included in this classification.

Heuristic and algorithmic approaches have only given attention to the problem associated with the design of the water-use system; effluent treatment and simultaneous systems design approaches have not been considered. Contributions in the field of water minimisation include those by Liu (1999), Dunn and co-workers (Dunn and Bush, 2001; Dunn and Wenzel, 2001) and Bagajewicz and co-workers (Bagajewicz et al., 1999, 2000; Savelski and Bagajewicz, 2001).

2.5 MATHEMATICAL PROGRAMMING TECHNIQUES FOR WATER SYSTEM DESIGN

Conceptual approaches to water system design have shown limitations in dealing with the more complicated systems, particularly those involving multiple contaminants. The use of mathematical programming for water system design overcomes these limitations and has found wide application in the field as a result. Conceptual approaches have however established some key concepts which have been carried over to the mathematical programming approach. This section considers the use of mathematical programming techniques for water system design. **Section 2.5.1** presents some introductory concepts in mathematical programming while **Section 2.5.2** examines some of the issues involved in the application of mathematical programming to the water system design problem. **Section 2.5.3** reviews the application of mathematical programming to the water minimisation problem while **Section 2.5.4** reviews the use of mathematical programming for wastewater treatment system design; the use of

mathematical programming for combined system design is considered in **Section 2.5.5**. The interpretation and representation of results from mathematical programming, as a means of delivering insight into the performance of the system, is reviewed in **Section 2.5.6**. Some concluding remarks on the use of mathematical programming for water system design are presented in **Section 2.5.7**.

2.5.1 Introductory Concepts in Mathematical Programming

According to a recent review by Wright (2000), the term mathematical programming was coined around 1945 and is synonymous with optimisation. In their review on the advances in mathematical programming with respect to process design and synthesis, Grossmann et al. (1999) identify three steps associated with the use of mathematical programming approaches to design, integration and operation problems. The first step involves the representation of the set of possibilities from which the optimal solution will be selected. The mathematical programming problem, which typically involves both continuous and discrete variables is formulated in the second stage while the third is concerned with the solution of the optimisation problem and the identification of the optimal solution.

Papadimitriou and Steiglitz (1982) classify optimisation problems according to whether they contain continuous variables or discrete variables. Those problems containing discrete variables (possibly in addition to continuous variables) are referred to as combinatorial problems. According to Grossmann et al. (1999), design and synthesis problems give rise to discrete/continuous optimisation problems, which, when represented algebraically, correspond to mixed-integer optimisation problems of the form:

$$\min Z = f(x,y)$$
$$\text{such that} \quad h(x,y) = 0$$
$$g(x,y) \le 0$$
$$x \in \mathrm{R};\ y \in \{0,1\} \qquad\qquad 2.3$$

where Z is the objective variable; $f(x,y)$ is the objective function (e.g. cost); $h(x,y) = 0$ is the set of equality relationships or constraints describing the performance of the system (e.g. mass-balances); $g(x,y) \le 0$ is the set of inequality relationships that describe the specifications or constraints which correspond to feasible choices for the system; x is the set of continuous variables; and y is the set of discrete variables, the values of which are restricted to zero or one. Continuous variables correspond to the selection of the operating levels for the system while discrete variables are associated with the selection of the system configuration in terms of the logical selection of an item or action or not. Some of the logical decisions covered by these constraints include: the selection of a single item, a maximum of one item, or at least one item; conditional selection, that is, if a particular item is selected, then a second item should also be selected; and, the activation and deactivation of continuous variables (Grossmann, 1996). The approach to formulating logical decisions is presented by Grossmann (1996) while the integration of logical decisions such that only the necessary constraints are included in the

model is considered by Raman and Grossmann (1993). Discrete variables are also referred to as binary variables or integer variables.

Depending on the nature of the constraints and the types of variables involved in the optimisation problem, different algorithms are required to solve the different optimisation problems which arise. Linear programming (LP) problems contain only continuous variables and the constraints and objective function are all linear. The solution techniques available for LP problems are guaranteed to find the global (as opposed to the local) optimum solution. Mixed-integer linear programming (MILP) problems contain both discrete and continuous variables but the objective function and the constraint equations remain linear. Solution algorithms for MILP problems are similarly guaranteed to converge to the global optimum. Should any of the constraint equations or the objective function in either the LP or MILP problems be nonlinear, these problems are designated as nonlinear programming (NLP) and mixed-integer nonlinear programming (MINLP) problems respectively. Solution methods for both NLP and MINLP problems are likely to converge to local optima which may or may not coincide with the global optimum; the exception to this is the case of convex NLP problems for which any local optimum is also the global optimum (Edgar et al., 2001). Problems containing only discrete variables are termed mixed-integer programming (MIP) problems.

The set of possibilities, amongst which the optimal solution is to be found, is typically postulated as a superstructure. More specifically, the superstructure allows a representation of the possibilities which can be screened in a systematic way such that the optimal solution can be determined. According to Grossmann (1996), Umeda et al. (1972) were probably among the first to propose the optimisation of superstructures for process synthesis. Grossmann et al. (1999) cite two major considerations in the formulation of the superstructure. The first consideration relates to the type of representation that could be used and the implications this would have on the modelling of the system. The second consideration involves the inclusion of all feasible possibilities within the selected representation such that the global optimum is not excluded from the analyses. A review on the postulation of superstructures for Process Synthesis is presented by Grossmann (1996).

In terms of the formulation of mathematical programming problems, Grossmann et al. (1999) identify three categories according to the level of detail included in the model. Aggregated models are high level representations of the system in which the associated problem is simplified by a particular aspect or objective which characterises the problem. Examples of aggregated models include the transshipment model used for HEN and MEN Synthesis; for MEN Synthesis, the transshipment problem represents the transport of a commodity (mass of species) from sources (species-rich streams), through warehouses (concentration intervals), to destinations (MSA streams) (Mann and Liu, 1999). Short-cut models include a greater level of detail in the superstructure for purposes of cost optimisation. Here, unit operations are modelled using simple nonlinear equations for reasons of avoiding excessive computational cost and possibly the exploitation of the algebraic structure associated with the equations. Rigorous models represent detailed superstructures in which the performance of unit operations is described by complex models. Grossmann et al. (1999) note that the aggregated models

often give rise to simpler types of optimisation problems in LP, NLP and MILP models, as opposed to MINLP problems which tend to arise from short-cut and rigorous models.

In solving mathematical programming models, Grossmann et al. (1999) identify two solution strategies, that is, simultaneous optimisation and sequential optimisation. Simultaneous optimisation involves the solution of a single problem in which all trade-offs are considered simultaneously. Sequential optimisation involves the solution of a sequence of sub-problems of increasing detail rather than a single large problem. Sequential optimisation is less rigorous than simultaneous optimisation; the sub-problems are however easier to solve.

2.5.2 Some Preliminaries on Mathematical Programming for Water System Design

Since the conceptual approach shows limitations where complex systems are involved, and particularly in the area of systems involving multiple contaminants, mathematical programming has become the method of choice for water-system design (Bagajewicz, 2000). However, the use of mathematical programming for water-system design is not without its own problems.

Typically, the set of candidate network designs is formulated as a superstructure comprising freshwater sources, wastewater sinks, unit operations, mixers and splitters (Figure 2.15). In this framework, each operation is preceded by a conceptual mixer and followed by a conceptual splitter. Each freshwater source is similarly followed by a conceptual splitter and each wastewater sink preceded by a conceptual mixer. The water demand for a particular operation is thus supplied by a combination of water from the freshwater sources and water from the operations within the system. The water emerging from the operations within the system is diverted to other operations within the system or sent to the wastewater sink. The use of the superstructure for the water minimisation problem is presented by several authors (Rossiter and Nath, 1995; Doyle and Smith, 1997; Alva-Argáez, 1999; Mann and Liu, 1999; Thevendiraraj et al., 2001, 2002). Kuo and Smith (1997), Galán and Grossmann (1998, 1999) and Alva-Argáez (1999) consider the use of superstructures for addressing the distributed wastewater treatment problem while superstructures featuring both water-using and water treatment operations have been proposed by a number of authors (Takama et al., 1980a,b; Alva-Argáez et al., 1998a,b; Alva-Argáez 1999; Huang et al., 1999a,b; Benkő et al., 1999, 2000; Brouckaert et al., 2001).

The optimisation of the superstructure is usually formulated as an NLP problem which may or may not involve discrete variables. The source of these nonlinearities is the contaminant material balance equations which involve bilinear terms arising from the multiplication of the water flowrate by contaminant concentration (Quesada and Grossmann, 1995). Bilinear terms are non-convex and result in the presence of several local optima in the solution space. The presence of these local optima makes the application of standard NLP techniques ineffective in determining the global optimum. In addition, numerical singularities arise when flows take on values of zero making it difficult for the NLP algorithms to converge to a feasible solution. Wright (2000) comments that there are a number of approaches available for global optimisation, but efficient implementation of these strategies is heavily dependent on the

exploitation of the structure of the problem under consideration; nevertheless, these methods remain computationally intensive. A review on global optimisation techniques is presented by Floudas and Pardalos (2000). Other reviews of note include a review of LP and NLP algorithms by Wright (2000) and reviews on MINLP algorithms by Grossmann and co-workers (Grossmann and Kravanja, 1995; Grossmann, 1996; Grossmann et al., 1999; Grossmann and Hooker, 2000).
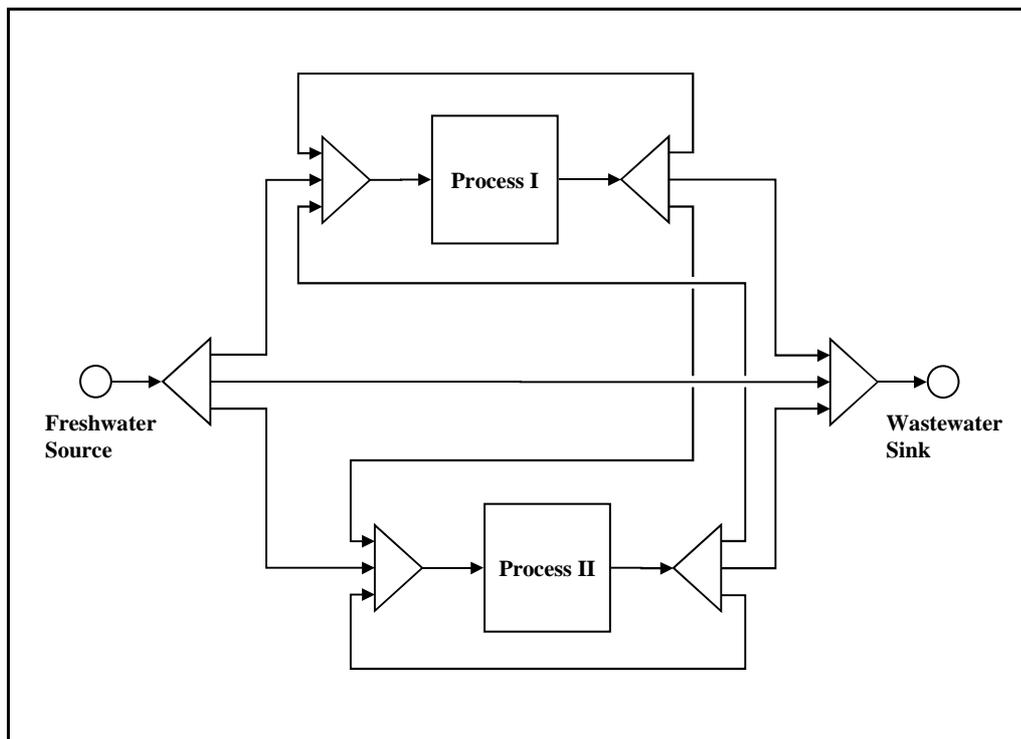
Figure 2.15. *An illustration of the superstructure concept as it pertains to water minimisation*

Despite not being able to determine the global optimum with certainty, achieving solutions which are seemingly coincidental to, or in the vicinity of the global optimum remain an important aspect of the use of mathematical programming for water system design. Edgar et al. (2001) comment that the performance of NLP solvers is strongly influenced by the point from which the solution process is initiated. Initial values for the variables which satisfy most of the constraints and which, if possible, are located in the same region of space as the global optimum are more likely to converge to the global optimum (GAMS Development Corporation, 2001). Other approaches however see the manipulation of the NLP problem such that LP algorithms, which guarantee global optimality, can be used. Examples of this type of approach include those by Vaidyanathan et al. (1998) and Jacob et al. (2002). Grossmann (1996) proposes measures which reduce the size of the superstructure and thus the solution space of the search. Such measures include the state-space approach introduced by Bagajewicz and Manousiouthakis (1992) and preliminary screening of alternatives.

2.5.3 Mathematical Programming for Water Minimisation

While the work of Takama et al. (1980a,b; 1981) is regarded by Bagajewicz as the seminal work in the application of mathematical programming to water system design in the industrial context (Bagajewicz, 2000), its consideration is deferred until **Section 2.5.5** since it considers the water-use and water treatment subsystems simultaneously.

The basic model for the water-use system comprises a number of freshwater sources of different quality and a number of water-using operations which are typically characterised by fixed mass-loads of contaminants transferred to the water, with concentration limits applied to the water entering and leaving the operations (Alva-Argáez, 1999). The objective of the synthesis problem is then to supply each of the water-using operations with water of suitable quality in the most efficient manner, whether this efficiency is measured in terms of total water use, operating cost or overall investment cost. It should be noted that where only a single water source is available, the operating cost minimisation problem is equivalent to reducing the amount of water used by the system (Doyle and Smith, 1997). The representation of the operations only in terms of the water-side of the problem relies on the concept of the limiting water profile, an insight gained from the conceptual approach (Doyle and Smith, 1997; Alva-Argáez, 1999).

In expressing this model mathematically, a mass-balance is carried out for each contaminant over each conceptual mixer and splitter and each operation in the system. Typical forms of these balances are:

Mixer Balances for Operations:

$$F_i^{in} = \sum_j F_{j,i} + \sum_w F_{w,i} \qquad\qquad 2.4$$

$$F_i^{in} \cdot C_{i,k}^{in} = \sum_j F_{j,i} \cdot C_{j,k}^{out} + \sum_w F_{w,i} \cdot C_{w,k} \qquad\qquad 2.5$$

Mixer Balances for Wastewater Discharge Points:

$$F_d = \sum_i F_{i,d} \qquad\qquad 2.6$$

$$F_d \cdot C_{d,k} = \sum_i F_{i,d} \cdot C_{i,k}^{out} \qquad\qquad 2.7$$

Splitter Balances for Operations:

$$F_i^{out} = \sum_j F_{i,j} + \sum_d F_{i,d} \qquad\qquad 2.8$$

Splitter Balances for Freshwater Sources:

$$F_w = \sum_i F_{w,i} \qquad\qquad 2.9$$

Balances across Operations:

$$F_i^{out} = F_i^{in} \qquad\qquad 2.10$$

$$\Delta m_{i,k} = F_i^{out} \cdot C_{i,k}^{out} - F_i^{in} \cdot C_{i,k}^{in} \qquad\qquad 2.11$$

where F_i^{in} and F_i^{out} are the inlet and outlet water flows associated with operation i; $F_{j,i}$ is the flow from operation j to operation i; $F_{w,i}$ is the flow of water from freshwater source w to operation i; $F_{i,d}$ is the flow from operation i to wastewater discharge point d; F_w is the total flow associated with freshwater source w; and F_d is the total flow of water associated with wastewater discharge point d. $C_{i,k}^{in}$ is the concentration of contaminant k at the inlet of operation i; $C_{i,k}^{out}$ and $C_{j,k}^{out}$ are the concentrations of contaminant k at the outlet of operation i and operation j; and $C_{w,k}$ is the concentration of contaminant k associated with freshwater source w. $\Delta m_{i,k}$ is the mass-load of contaminant k transferred to the water over operation i. Equation 2.9 is written for all freshwater sources while Equation 2.6 and 2.7 are written for all wastewater discharge points. Equations 2.4, 2.5, 2.8, 2.10 and 2.11 are written for all mass-exchange type operations. The maximum contaminant concentration limits applied to the inlet and outlet contaminant concentrations respectively, take the form:

$$C_{i,k}^{in} \leq C_{i,k}^{in,max} \qquad\qquad 2.12$$

$$C_{i,k}^{out} \leq C_{i,k}^{out,max} \qquad\qquad 2.13$$

where $C_{i,k}^{in,max}$ and $C_{i,k}^{out,max}$ correspond to the maximum inlet and outlet concentration limits for contaminant k in operation i.

It should be noted that the Equations 2.4 to 2.13 are not taken directly from any particular source and correspond to generic versions of those presented in (Takama et al., 1980a,b; Doyle and Smith, 1997; Alva-Argáez, 1999); their inclusion within this review is to create a context for the discussion of approaches used in dealing with the water minimisation problem. The formulation of the model is completed by the inclusion of a suitable objective function. For the minimisation of operating cost, this takes the form:

$$Z = \sum_w CST_w \cdot F_w + \sum_d CST_d \cdot F_d \qquad\qquad 2.14$$

where Z is the operating cost; CST_w is the cost factor associated with the purchase of freshwater source w and CST_d is the cost factor associated with the use of wastewater discharge point d.

Equations 2.4 to 2.14 correspond to an NLP formulation of the water minimisation problem. The balance over the water-using operation establishes a relationship between the flowrate and quality of the water entering the operation and the flowrate and quality of water leaving the operation (Equations 2.10 and 2.11). One approach to applying LP to the water minimisation problem involves fixing the total water flow to and from each operation and the outlet concentrations from each operation. This results in Equation 2.5 becoming linear and circumvents the need for Equations 2.10, 2.11 and 2.13. This approach is applied by Vaidyanathan et al. (1998) and Jacob et al. (2002) who conceptualise the system as being made up of water sources of fixed quantity and quality and demands with fixed water flow requirements and maximum concentration limits. Nobel and Allen's (2000) use of GIS (Geographic Information System) software for determining the optimal reuse strategy for industrial wastewater-reuse on a regional basis amounts to the same problem. Here LP is used to determine the optimal allocation of water from industrial sources of fixed quality and quantity to demands with fixed water requirements and quality limitations in a geographic region rather than an individual industrial site.

A similar conceptualisation of the problem in terms of water sources and water demands is presented by Shafiei et al. (2001) but a genetic algorithm is used in conjunction with linear programming to determine the optimal water management strategy for a pulp and paper mill. This formulation further seeks to minimise the fibre-loss from the system in addition to the reducing the amount of water used; fibre is a desirable component in the paper industry.

Doyle and Smith (1997) use a slightly different approach to linearising the NLP problem formulation; their motivation for linearising the problem is however to generate a suitable starting point for the solution of the NLP problem. According to this approach, the outlet concentrations from the operations are set at their maximum values and Equation 2.11 is changed to an inequality, given that water may enter the operation at a concentration lower than the limiting inlet concentration. Given that the left-hand side of Equation 2.11 is determined by the process-side of the operation and is thus a fixed value, Equation 2.11 will only be feasible if it is possible for the right-hand side to be greater than the left-hand side and hence the inequality.

Bagajewicz and Savelski (2001) use the necessary conditions of optimality for single contaminants (Savelski and Bagajewicz, 2000) to convert the NLP problem formulation to an LP formulation. The necessary conditions of optimality comprise a set of theorems formulated and proven initially for systems involving single contaminants which guarantee the global optimum solution to the problem associated with the design of the water-use network for systems involving mass-exchange type operations. Bagajewicz and Savelski (2001) eliminate the bilinearities in the equations using the necessary condition of maximum outlet concentrations for the operations present in the system and the conversion of certain equalities to inequalities through the incorporation of Equation 2.12 into the appropriate mass-balance equations. This linearisation of the problem forms the first step of a two-step approach for the design of the water-use system. In the second step, the number of connections is minimised via an MILP problem formulation which incorporates the minimum freshwater flow target, as

determined from the first step, as a constraint. Two other objective functions for the MILP formulation are considered – one which minimises the fixed annualised cost while the other gives attention to forbidden and compulsory matches, which are significant in the retrofit problem. The approach is extended to consider the inclusion of a regeneration process and a linear formulation of this problem is presented. The same approach is presented and applied by Dericks et al. (2001).

Linear programming is used in a slightly different way by Bagajewicz et al. (1999) in determining the optimal allocation strategy for a system of water-using operations involving multiple contaminants. This approach is an extension of the maximum reuse algorithm presented previously for single contaminants (Savelski and Bagajewicz, 1999; 2001) and relies on the necessary conditions for optimality as presented for multiple contaminants. Here a linear programming step is incorporated into the algorithm to account for the presence of multiple contaminants such that the amount of freshwater required by the evolving network is minimised as the algorithm proceeds.

Rossiter and Nath (1995) consider the solution of the NLP problem formulation without manipulating it such that it becomes an LP problem. These authors comment that while the approach is not guaranteed to locate the global optimum, its location is relatively easy to find in problems not involving regeneration. Where regeneration is involved, multiple starting points are recommended as a way of finding the global optimum. It should be noted that here, knowledge of the location of the global optimum is derived by comparison of the solutions obtained via mathematical programming and those obtained using the conceptual approach. Multiple initialisations as a method of locating the global optimum is also recommended by Edgar et al. (2001).

The solution of the water minimisation problem via NLP is also considered by Mann and Liu (1999) and Dunn et al. (2001). The model considered by Dunn et al. (2001) is an extension of the LP model presented by Vaidyanathan et al. (1998) but it becomes nonlinear due to some of the sinks being able to accept variable as opposed to fixed water flowrates. Consideration of the presence of a regeneration process is given by Mann and Liu (1999).

Alva-Argáez (1999) formulates the water minimisation problem as an MINLP problem which includes integer constraints in the formulation. Using the insight, gained from the conceptual approach to water minimisation, that the concentration of at least one of the contaminants will have reached its limiting value in the optimal solution, the problem is solved via a decomposition procedure which sees the successive solution of two sub-problems. In the first sub-problem, the outlet contaminant concentrations for all contaminants are set at their limiting values and slack variables are introduced to account for contaminants which do not reach their limiting concentration; this formulation is thus an MILP problem which is solved to global optimality. The second sub-problem is an LP problem which seeks to update the outlet concentrations of the contaminants which were set at their limits in the first sub-problem. The contaminant outlet concentrations obtained from the solution of this second sub-problem are used in the first sub-problem in the succeeding iteration. Iterations continue until a tolerance

criterion has been met. It has been noted by Bagajewicz (2000) that the solution procedure is similar to that of Takama et al. (1980a,b; 1981).

A completely different approach to the water minimisation problem sees the problem being formulated as a transshipment problem. Mann and Liu (1999) present a model which is equivalent to that proposed earlier by El-Halwagi and Manousiouthakis (1990b) for MEN Synthesis. Alva-Argáez et al. (1999) present a transhippment model for the water minimisation problem for a system involving multiple contaminants.

2.5.4 Mathematical Programming for Wastewater Treatment

Some of the early developments in the application of mathematical programming to the design of wastewater treatment systems are reviewed by Mishra et al. (1975). In this review, three types of studies are identified, namely unit process design, process subsystem design and complete system design. Unit process design refers to the design of individual process units. Process subsystem design extends to the design of a certain stage of the treatment system. As such, it deals with more than one individual process and the interactions between these operations. The complete system design considers the design of more than one subsystem, together with the sequencing of these subsystems and the interactions between them, in forming the treatment system capable of meeting the required effluent discharge criteria. It is pointed out that the studies concerned with system design have tended to optimise a fixed structure of multiple stages although a few studies have included the possibility of stream branching and recycle.

Kuo (1996) is credited as the first author to suggest the formulation of the wastewater treatment problem as a superstructure (Alva-Argáez, 1999). Superstructure formulations are also presented by Galán and Grossmann (1998; 1999) and Alva-Argáez (1999). Galán and Grossmann (1998) outline the problem as follows:

Given a set of process liquid streams of known flowrate and pollutant concentrations and a set of technologies of differing performance and treatment costs which is capable of removing the pollutants, identify the interconnections of technologies and the corresponding flowrates which will achieve the required discharge specifications at minimum cost.

Galán and Grossmann (1998; 1999) formulate this problem as an NLP problem and use a heuristic search procedure together with mathematical programming to locate the global optimum. In motivating this approach, it is pointed out by the authors that the basic procedure for rigorous global optimisation involves a spatial branch and bound algorithm which relies on the use of linear underestimators as approximations for the bilinear terms. While these methods are computationally intensive, the global optimum is often located from the initial relaxation, with the remainder of the effort being spent confirming the optimality of this initial solution. The heuristic procedure, however, circumvents this problem by solving a relaxed LP formulation of the problem with different objective functions, as a means of generating a range of starting points for solving the NLP formulation. The relaxed LP formulation of the problem

used is that presented previously by Quesada and Grossmann (1995) for the global optimisation of networks comprising splitters and mixers and involving multiple component streams. In this formulation, the bilinearities are eliminated from the model by exploiting the maximum and minimum limits on the flows and concentrations. The solution obtained via the heuristic search approach to global optimisation (Galán and Grossmann, 1998; 1999) is compared with that obtained by rigorous global optimisation by Zamora and Grossmann (1998) and shown to be similar. In an extension to the original formulation, Galán and Grossmann (1998) present an MINLP formulation for the problem which includes integer constraints for the selection of treatment operations among different candidate treatment technologies.

The solution approach presented by Alva-Argáez (1999) for the design of the distributed wastewater treatment network is similar to that proposed previously for the design of the water network (Alva-Argáez, 1999). The decomposition approach is however slightly more complicated with the inclusion of a penalty function into the first sub-problem, the value of which is increased after each iteration.

The design of distributed wastewater treatment networks via mathematical programming is also addressed by Mann and Liu (1999) who consider an NLP formulation of the problem.

2.5.5 Mathematical Programming for Combined Systems

This subsection addresses the application of mathematical programming to the design of systems featuring both water-using and water treatment operations. Before addressing the industrial situation as presented initially by Takama et al. (1980a,b; 1981) mention should be made of some of the other applications of mathematical programming to water system design.

Bishop and Hendricks (1971) present an LP transshipment model for water-reuse planning at a regional level. The scope of the problem extends to determining the optimal allocation of water between different origins and user sectors with water treatment being applied if necessary. Consideration of the costs associated with water transport and treatment are included in the formulation. In their consideration of the problem, Pingry and Shaftel (1979) present a NLP formulation of the water-reuse planning problem for water management at a regional level. These authors point out that in many previous models, water quality is not given explicit consideration in the selection among several recycling configurations. In this formulation of the water-reuse planning problem, the quality of the water is explicitly considered and the possibility of recycling amongst treatment operations, water-users and disposal sites is included. The model is reformulated as a transhippment problem and solved; some degree of linearisation is suggested and a solution algorithm, which involves the successive solution of LP problems, presented. The water-reuse planning problem at a regional level is also considered by Ocanas and Mays (1981). This formulation, proposed and solved as an NLP problem, considers the recycle of water to its origin; in effect sources and discharge points are thus the same.

Takama et al. (1980a) consider the application of mathematical programming to industrial systems comprising both water-using and water treatment operations and involving multiple contaminants. The water-using operations are characterised by a fixed contaminant mass-load addition while the treatment operations are characterised by a contaminant removal ratio. In their first publication (Takama et al., 1980a), a direct search method, termed the complex method, is used to solve the problem. This method involves the transformation of the problem into a sequence of modified problems without inequality constraints and the introduction of a penalty function effective for those contaminant concentrations not complying with their maximum limits. During the course of the optimisation, the value of the penalty function is increased and simultaneously, uneconomical features of the network removed. It is noted however that exclusion of uneconomical features of the network at each step may lead to topology traps (Alva-Argáez et al., 1998a). In a subsequent publication, Takama et al. (1980b) point out that the direct search method proposed in their previous publication is limited to relatively small problems and propose an iterative LP approach to dealing with larger problems. The approach is described in a more formal mathematical context in Takama et al. (1981).

In considering the application of mathematical programming to the combined system, Alva-Argáez et al. (1998b) note that the route to water minimisation is via reuse, regeneration reuse and regeneration recycle. It should be pointed out that the only route to water minimisation where no treatment/regeneration operation is present is via reuse which may include direct recycle as illustrated in Figure 2.15. The combined problem involving water-using and water treating operations (Alva-Argáez et al., 1998b; Alva-Argáez, 1999) is formulated as an MINLP problem and solved using the approach presented previously for the water minimisation and distributed effluent treatment design problems.

Benkő et al. (1999, 2000) formulate the problem involving water-using operations and treatment operations as an NLP problem. The proposed solution strategy involves the use of two different NLP algorithms, with the solution obtained from the use of the one algorithm serving as the initialisation point for the other.

In their consideration of the problem involving water-using and water treatment operations, Huang et al. (1999a,b) present a modified version of the superstructure presented by Takama et al. (1980a,b) which includes multiple water sources and water sinks. The possibility of a water loss, which may occur at any concentration, is included in the unit operation model for both water-using and water treatment operations. In addition, the notion of reacting solutes is recognised via the inclusion of a fixed mass-load term in the unit operation model; this mass-load term is however equivalent to the usual contaminant mass-load addition term included in the standard mass-exchange model. The problem is formulated as an NLP and solved using standard NLP algorithms.

The study by Brouckaert et al. (2001) into the optimal placement of membrane treatment facility in a power station via mathematical programming similarly considers both the

water-using and water treating subsystems simultaneously. The problem is formulated and solved as an NLP problem.

2.5.6 Interpretation and Representation of Results from Mathematical Programming

A common criticism of the mathematical programming approach and one made by several authors is that while it provides answers to problems associated with water system design, it does not provide the insight into the performance of the system that the conceptual approach offers (El-Halwagi, 1995; Buehner and Rossiter, 1996; Dhole et al., 1996; Doyle and Smith, 1997; Mann and Liu, 1999; Ponton, 1999). To overcome this problem, the trend is towards the construction of graphical representations of the system or composite curves which are derived from the mathematical programming solution. Bagajewicz (2000) notes that this sees a change in the function of the composite curves; where previously they were used to predict targets for the system, in this role they provide insight into the performance of the system.

Doyle and Smith (1997) present a methodology to represent the solution obtained via mathematical programming for the water minimisation problem involving mass-exchange type operations and multiple contaminants on a set of graphical axes. The approach is based on the selection of a reference contaminant and involves concentration shifting for other contaminants relative to this reference. It is however not evident from this construction which of the contaminants have reached their limits. Wenzel et al. (2002) present a tabular representation in which the suitability of matches between sources and sinks is tracked in terms of the contaminants carried by the sources. Different symbols are used to indicate whether a single component is limiting or multiple components are limiting.

A common practice adopted by some commercial computer software (Linnhoff March Limited, 2001; American Process Inc, 2002) for representing the mathematical programming solution graphically is to represent it via the source and sink purity profiles introduced by Buehner and Rossiter (1996) and Dhole et al. (1996). These curves are plotted separately for each contaminant. The UMIST software WATER presents the *shifted* profiles as presented by Doyle and Smith (1997) (Thevendiraraj et al., 2002).

Other insights into the sensitive areas of the system are however also available from the mathematical programming solution via the marginal values (Brooke et al., 1998; Mann and Liu, 1999). These values give a measure of what the effect would be on the objective variable if the value of a particular constraint, for example, a particular contaminant concentration limit, were to be changed by a small amount. This information provides insight into those areas of the system which have the greatest impact on the objective function, whether it be cost or water-consumption based. The use of sensitivity indicators is also highlighted by Rossiter and Nath (1995), Tainsh and Rudman (1999), Nobel and Allen (2000) and Linnhoff March Limited (2001).

2.5.7 Concluding Remarks on Mathematical Programming for Water System Design

A number of other studies involving the use of mathematical programming for water system design, whether by commercial packages which serve as a front end to the mathematical programming software or not, have been reported. These references include those by Tripathi (1996); Paris (1998), Baetens and Tainsh (2000), Koufos and Retsina (2001), Malpei et al. (2000), Thevendiraraj et al. (2001, 2002), Brouckaert et al. (2002) and Schneider (2002). Consideration of the application of mathematical programming to water minimisation for systems involving batch operations is presented by Almató et al. (1997; 1999a,b), Puigjaner et al. (1999; 2000), Majozi et al. (1998a,b) and Majozi (1999).

Jödicke et al. (2001) comment that the methods for determining the optimal water system design require a large amount of data to be collected and frequently suggest a design which is rejected due to factors which were not considered in the analysis, or due to prohibitive capital costs. To overcome this obstacle, these authors propose an MILP model which uses data which is easily available on the plant, requiring only the location of the process, its current water demand and binary information on the reuse potential of water from the various sources and sinks within the system. This binary information is expressed as a connectivity matrix of ones and zeroes with a one representing the possibility of a particular water source being used for a particular sink. The model attempts to minimise the operating cost (freshwater, wastewater treatment and pumping) and investment costs (piping and holding tanks). The assumption is made that all wastewater has to pass through a holding tank prior to reuse which increases the possibility that the resulting network design will be robust. It should be noted that the superstructure for this model is completely different to that presented in Figure 2.15. As such, the superstructure comprises two parts: one part describes the possible piping from the water sources to the tanks while the other describes the possible piping from the tanks to the water sinks.

2.6 COMBINED RESOURCE SYSTEM DESIGN

Multiple resources are usually required by a chemical process system for the transformation of raw materials to products. The optimal design of combined resource systems has started to gain some attention as a result. This subsection reviews the developments in this research area. **Section 2.6.1** considers the developments in combined resource system design in MEN Synthesis while **Section 2.6.2** reviews the developments in thermal-water system design. **Section 2.6.3** reviews the area of Combined Water-Oxygen Pinch Analysis.

2.6.1 Combined Resource System Design and MEN Synthesis

In the context of mass-exchange networks, Srinivas and El-Halwagi (1994b) give consideration to systems in which temperature targets accompany the mass-exchange targets. Here, the task

involves the synthesis of a mass-exchange network which can preferentially transfer a certain species from a set of rich streams to a set of lean streams while simultaneously achieving a specific heat transfer task in a cost-effective manner. Combined mass and energy integration is also considered by Papalexandri and Pistikopoulos (1995).

2.6.2 Thermal-Water System Design

Recently the design of water-use networks involving other resources in addition to water has been considered. The approaches presented in **Section 2.3** to **Section 2.5** do not include temperature as a consideration in producing a design for the water system. It has however been suggested, though not applied, that heat content could be treated as a contaminant (Baetens and Tainsh, 2000). Savulecu (Savulescu, 1999; Savulescu and Smith, 1999; Savulescu et al., 2001, 2002) presents a graphically based conceptual approach for the design of a water system involving mass-exchange operations which require water at a range of temperatures. Initially isothermal operation of the different process operations is assumed, but the approach is extended to include operations with heat and water losses (Savulescu, 1999). The dual role of steam as a heating utility and a water source is considered (Savulescu, 1999). The use of mathematical programming for solving the problem is considered by Savulescu (1999), who presents an MILP formulation of the problem, and Bagajewicz et al. (2002), who present an approach comprising an LP problem, which uses the necessary conditions of optimality (Savelski and Bagajewicz, 2000), and a heat transhippment model. This approach utilises the state-space approach introduced by Bagajewicz and Manousiouthakis (1992).

Combined water and energy integration is also considered by Koufos and Retsina (2001). Consideration of the design of distributed effluent cooling systems for effluent temperature reduction is presented by Savulescu (1999), Kim et al. (2001) and Kim and Smith (2001).

2.6.3 Combined Water-Oxygen Pinch Analysis

The notion of combined water-oxygen pinch is presented by Zhelev and co-workers (Zhelev and Bhaw, 1999; Zhelev and Ntlhakana, 1999). Oxygen pinch is concerned with the optimal utilisation of oxygen for more cost effective wastewater treatment. It is noted by Zhelev and Bhaw that the application of Water Pinch Analysis results in a decrease in the wastewater flow and therefore volumetric cost but a degradation in the wastewater quality. With the cost associated with wastewater treatment being inversely proportional to the quality, this degradation results in an increase in costs. The application of a combined methodology allows these competing effects, that is, savings from wastewater volume reduction versus additional costs due to wastewater degradation, to be considered simultaneously.

2.7 OPTIMISATION OF SYSTEMS WITH DESIRABLE AND/OR REACTIVE SPECIES

Of the reported instances of desirable species being present within the water system, it is the cases from the pulp and paper industry (Sorin and Bédard, 1999b; Bédard and Sorin, 2000; Shafiei et al., 2001; Jacob et al., 2002) that predominate in terms of the attempts made to include these factors alongside the water minimisation problem. While Sorin and Bédard (Sorin and Bédard, 1999b; Bédard and Sorin, 2000) take note of the value of fibres and fines, these factors are not included in the targeting procedure. Shafiei et al. (2001), through the application of their genetic algorithm in conjunction with LP, arrive at solutions which feature superior fibre conservation in addition to water minimisation. It is however not clear whether fibre-loss is rigorously targeted. Jacob et al. (2002) make allowance for the targeting of fibre-loss within their LP formulation of the water minimisation problem. The fibre is however subject to maximum constraint limits in all operations which is equivalent to the constraints for the other contaminants.

Parthasarathy (2001) considers the problem associated with minimising the cost of recycling in chemical processes. Streams recycled to the various process units usually have to meet certain process requirements such as flowrate and composition. The focus of the work is thus directed towards determining the minimum amount of fresh materials to be added to the recycled stream such that these process requirements are satisfied. Parthasarathy conceptualises the system as being made up of sources and sinks. It is noted that in practice, the flowrates and compositions of sources and sinks can fluctuate and as such it is more appropriate to describe an operating range for each source and sink. An NLP formulation of the problem is proposed for the minimisation of the cost of multiple sources. This problem is solved via a two-level strategy. The one level involves the transformation of the problem into an LP formulation via the fixing of flowrates and compositions for the sources and sinks while the other involves determining the appropriate levels at which these flowrates and compositions should be set.

Gardner's study on the chlor-alkali industry (Gardner, 1999) involves species which are both reactive and desirable. In particular, the species HCl (hydrogen chloride) and NaOH (sodium hydroxide) cannot coexist within the same stream. However, it was recognised that effluents carrying these species could potentially be reused within the system; given the economic value of these reagents relative to water, the recovery of these effluents was desirable. To overcome the reactivity problem, Gardner proposed a decomposition of the system into three divisions: one comprising streams and operations tolerant of HCl; one comprising streams and operations tolerant of NaOH; and, one comprising the other operations and streams. An iterative graphical targeting approach was proposed as a means of determining the freshwater and concentrated reagent (HCl or NaOH) target for the system. The design of the network satisfying the freshwater and reagent target evolves from the graph.

While reactivity of species carried by the water is recognised by Huang et al. (1999b) no specialised treatment of these aspects is given in the formulated model which represents the reaction via a fixed mass-load term. The study conducted by Brouckaert et al. (2001) into the optimal placement of a membrane treatment plant at a power station however deals with a number of aspects related to the reactivity of species. In this study, sodium, calcium, chloride and sulphate are considered as contaminants. Within the model for the process system, the cooling circuit, the ion-exchange plant and the reverse osmosis plant are considered as process models in the analysis. Water from the cooling circuit is exposed to the atmosphere and thus continuously absorbs carbon dioxide. Lime softening, which involves the addition of calcium hydroxide to the water, is used to control the concentration of carbonate in the cooling system via the precipitation of calcium carbonate. With the absorption of carbon dioxide from the atmosphere being fixed, a fixed amount of lime is required for softening. With the amount of carbonate removed being determined according to the solubility product of calcium carbonate, the concentration of calcium and carbonate are fixed for the cooling circuit, and hence this process model is represented using a fixed outlet concentration for calcium. Another solubility product consideration is present in the reverse osmosis model. The reverse osmosis plant produces a good quality permeate and a poor quality retentate from the influent water. As such, the operation of the membrane plant requires that no precipitation of calcium sulphate occur on the membranes. This is controlled by the introduction of a constraint of the form:

$$[Ca^{2+}] \cdot [SO_4^{2-}] \leq K_{sp,CaSO_4} \qquad\qquad 2.15$$

where $[Ca^{2+}]$ is the molar concentration of calcium, $[SO_4^{2-}]$ is the molar concentration of sulphate and $K_{sp,CaSO4}$ is the solubility product for calcium sulphate. In his review of the field, Bagajewicz (2000) cites operations with outlet concentrations controlled by solubility limit considerations as being an area in which additional research is required.

The ion-exchange process involves the reaction between cations removed from the influent stream and anions from the ion-exchange resin and vice versa. As the process proceeds it becomes necessary to regenerate the ion-exchange resin. As such, the greater the concentration of ions to be removed in the influent stream to the ion-exchange process, the greater cost incurred through regeneration chemicals used and effluent generated. This situation is dealt with by determining an equivalence between the load of ions in the influent water and the cost of removing that load in terms of regeneration and effluent production. This operation is thus an example of a situation in which cost (regeneration chemicals and effluent production) is proportional to effluent load, that is the concentration of ions in the influent water.

Apart from its contribution in the area of systems involving reactive species, a few other points should be noted from the study conducted by Brouckaert et al. (2001). Firstly, instead of being solely concerned with freshwater and wastewater reduction, this study seeks to determine the optimal location of a membrane treatment operation. A second point relates to the use of a connectivity matrix of ones and zeroes indicating the permissibility of connections between

particular sources and sinks; this is used as a tool to eliminate those connections which are known to be infeasible from the problem.

2.8 CONCLUDING REMARKS

This chapter has reviewed the concepts and literature on the field of water system design. Subsequent chapters will draw on these concepts as an approach is established for dealing with desirable and reactive species which accompany the undesirable contaminants present within the chlor-alkali complex. While this approach uses mathematical programming, the conceptual understanding of the problem remains important, particularly with reference to the interpretation of the results and the significance of the pinch for systems involving desirable and undesirable species.

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THE CHLOR-ALKALI COMPLEX

The application of Pinch Analysis to water and wastewater management at the Sasol Polymers chlor-alkali complex was first proposed as part of a project funded by the Water Research Commission of South Africa (WRC Project No. 851) (Brouckaert and Buckley (2002). As part of this project, a Water Pinch Analysis study at the chlor-alkali complex was conducted by Gardner and commenced in 1997 (Gardner, 1999). Motivated by the results from this study and with a number of process changes having been effected to the chlor-alkali complex, the follow-up study commenced at the start of 1999. This chapter provides an introduction to the chlor-alkali complex and considers the Water Pinch Analysis problem presented by the chlor-alkali system. Section 3.1 presents a description of the chlor-alkali complex and examines the way in which water is used within the complex. Section 3.2 reviews the initial Water Pinch Analysis study and highlights the changes which have been effected to the chlor-alkali complex since this study. Section 3.3 presents a detailed analysis of the system in the context of the applicability of the current Water Pinch Analysis theory and tools. Finally, some concluding remarks on this chapter as it relates to the objectives of this study are presented in Section 3.4.

3.1 THE SASOL POLYMERS CHLOR-ALKALI COMPLEX

The Sasol Polymers chlor-alkali complex comprises a number of smaller plants producing a range of products. **Section 3.1.1** presents a brief history of the chlor-alkali complex while the various plants which make up the chlor-alkali complex are described in **Section 3.1.2**.

3.1.1 A Brief History and Introduction

The Sasol Polymers chlor-alkali complex, formerly operated by Polifin Limited and previously by AECI Chlor-Alkali and Plastics Limited, is located within the Umbogintwini Industrial Site some 25 km south of Durban, South Africa. During its period of operation, which extended from 1955 to 2001, the complex produced chlorine and caustic soda, together with a range of other derived products. It was also in this period that the complex underwent a number of changes as processes were upgraded and decommissioned. As it stood at the time of its

closure, the complex produced caustic soda, chlorine, hydrogen, hydrochloric acid and sodium hypochlorite. It should be noted that unless otherwise indicated, references to the plant refer to its configuration as it stood at the point of closure.

3.1.2 Complex Description

Figure 3.1 presents a schematic diagram of the various plants which make up the Sasol Polymers chlor-alkali plant at Umbogintwini. Central to the activities of the complex is the brine circuit which converts raw salt to caustic soda, chlorine and hydrogen. Part of the chlorine and hydrogen generated from the circuit is used for the production of hydrochloric acid in the hydrochloric acid synthesis plant. Chlorine is further utilised, along with caustic soda, in the manufacture of sodium hypochlorite in the sodium hypochlorite synthesis plant. Two other plants located within the complex are the demineralisation plant, which produces a high quality water for use within the complex, and the Hydecat destruction plant which destroys surplus or below-specification sodium hypochlorite along with other chlorine-containing effluents.

Figure 3.1. *Schematic diagram of the Sasol Polymers chlor-alkali complex at Umbogintwini showing the interdependencies between the different plants on the complex.*

A brief description of the plants which constitute the chlor-alkali complex is presented below. The order of presentation of these plants is as follows: the brine circuit (**Section 3.1.2.1**); the hydrochloric acid synthesis plant (**Section 3.1.2.2**); the sodium hypochlorite synthesis plant (**Section 3.1.2.3**); the Hydecat destruction plant (**Section 3.1.2.4**); the demineralisation plant (**Section 3.1.2.5**); and, miscellaneous operations (**Section 3.1.2.6**). Reconciled mass-balances and block diagrams for these plants are provided in **Appendix A**.

3.1.2.1 *The Brine Circuit*

Figure 3.2 presents a simplified process flow diagram of the brine circuit. The electrolyser is the core process of the circuit and the operation in which sodium chloride is converted to chlorine gas and caustic soda, with hydrogen gas being generated simultaneously. The electrolyser is preceded by a series of raw material purification operations (precipitation, clarification, filtration and ion-exchange) which condition the brine solution to a standard acceptable to the electrolyser. The electrolyser is followed by various product processing operations (chlorine processing, hydrogen processing and caustic evaporation) and brine recycle conditioning operations (physical and chemical dechlorination and resaturation).
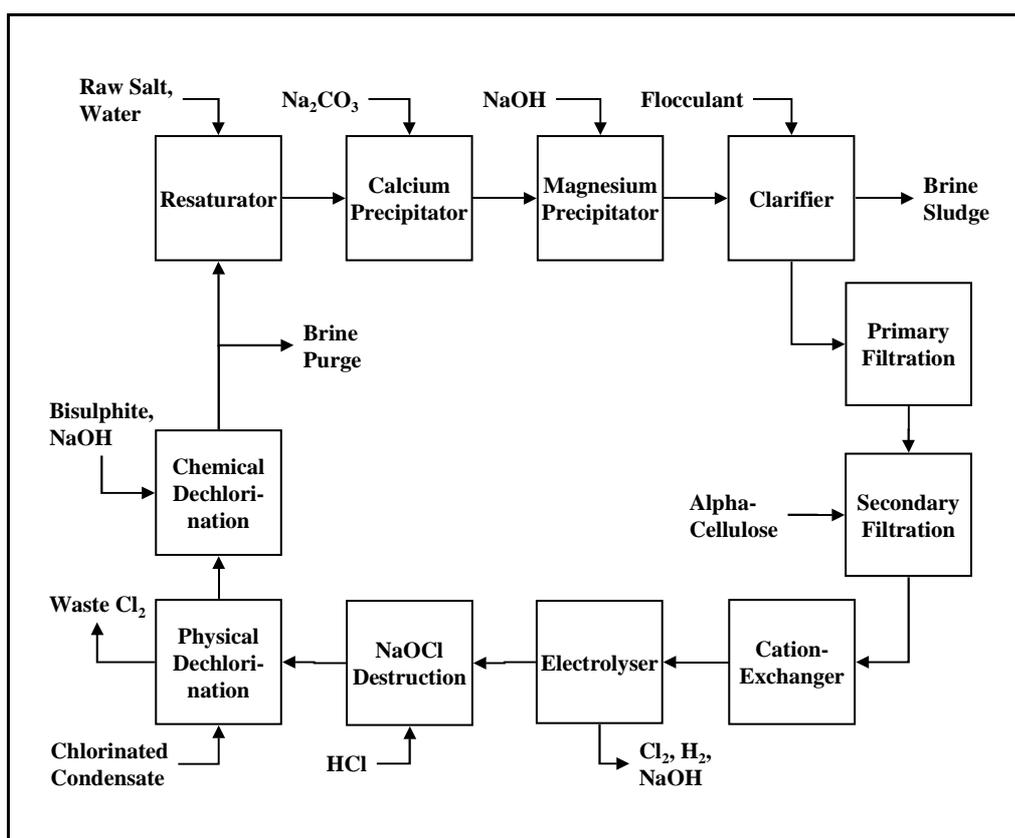
Figure 3.2. *Schematic diagram of the brine circuit at the Sasol Polymers chlor-alkali complex at Umbogintwini.*

Raw Material Purification

Raw salt is dissolved in a solution made up of recycled brine and demineralised water in the resaturator. The salt contains predominantly sodium chloride but also some trace impurities, amongst which are calcium and magnesium cations. Brine from the resaturator (~25% m/m NaCl) passes through the calcium precipitator, where dilute sodium carbonate (~16% m/m Na$_2$CO$_3$) is added to precipitate the calcium as calcium carbonate, and the magnesium precipitator, where dilute caustic soda (18% m/m NaOH) is added to precipitate the magnesium as magnesium hydroxide. A flocculant is added ahead of the clarifier where the precipitated material is removed from the brine stream as brine sludge. The clarified brine passes through the anthracite filters (primary filtration stage) where residual insoluble matter and precipitate (not removed by the clarifier) and a small quantity of the remaining calcium and magnesium are removed. This filter is backwashed periodically with polished brine and the backwash stream returned to the precipitation stage. The filtered brine passes through the brine polishing filters (secondary filtration stage). These filters use alpha-cellulose as a filter aid and small residual quantities of calcium and magnesium are removed. The polished brine is heated before it enters the ion-exchanger where the calcium and magnesium concentrations are reduced to levels acceptable to the electrolyser. The ion-exchanger consists of two cation-exchange resin beds arranged in series. During the normal cycle of operation (ion-exchange), the following metal cation removal reaction occurs:

$$2NaX + M^{2+} \rightarrow MX_2 + 2Na^+ \qquad\qquad 3.1$$

where X represents a structural unit of the cation-exchange resin and M^{2+} represents a divalent cation. NaX is the cation-exchange resin in the sodium form and MX_2 is the cation-exchange resin in the divalent cation form. Regeneration of each cation-exchange resin bed occurs every 72 h.

The Electrolyser

The electrolyser consists of three banks of membrane cells arranged in parallel. The conversion of sodium chloride to chlorine proceeds at the anode as follows:

$$2NaCl \rightarrow Cl_2 + 2Na^+ + 2e^- \qquad\qquad 3.2$$

and the anolyte (brine solution) decreases in strength as the reaction proceeds. The chlorine evolved at the anode is sent to chlorine processing.

The anode is separated from the cathode by a selectively permeable membrane which allows the migration of sodium cations from the anode to the cathode. At the cathode, the following reaction occurs:

$$2Na^+ + 2H_2O + 2e^- \rightarrow 2NaOH + H_2 \qquad\qquad 3.3$$
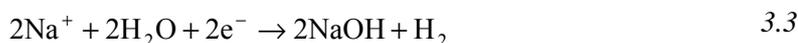
and the catholyte (caustic soda solution) increases in strength as the reaction proceeds. The caustic soda produced at the cathode (~32% m/m NaOH) is either sent to caustic evaporation, used within the plant, or diluted and recycled to the membrane cells. The hydrogen evolved at the cathode is sent to the hydrogen processing operations.

Alongside the reaction which produces chlorine, chlorates and hypochlorites are generated via side-reactions. Hypochlorites are generated within the electrolyser via:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$
3.4

$$HOCl \leftrightarrow H^+ + OCl^-$$
3.5
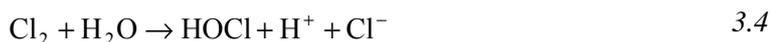
Chlorates are generated via:

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2H^+ + 2Cl^-$$
3.6
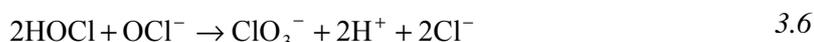
and to a lesser extent, electrochemically at the anode:

$$6OCl^- + 3H_2O \rightarrow 2ClO_3^- + 6H^+ + 4Cl^- + 1.5O_2 + 6e^-$$
3.7
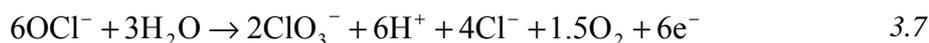
The level of chlorate in the circuit is controlled by a purge stream while the level of hypochlorite is controlled by the dechlorination operations.

Raw Material Conditioning

The depleted brine solution (~20% m/m NaCl) leaving the electrolyser is saturated with dissolved chlorine and chlorine-releasing species (hypochlorites), and is mixed with chlorine-containing condensate from the chlorine processing operations. The cation-exchange resin is extremely sensitive to oxidising species and all chlorine and chlorine-releasing species must be eliminated before the brine is recycled to the ion-exchanger.

Dechlorination is carried out in two stages. In the primary stage, concentrated hydrochloric acid (31% m/m HCl) is dosed to the brine such that chlorine is liberated from the chlorine-releasing species:

$$2HCl + NaOCl \rightarrow NaCl + Cl_2 + H_2O$$
3.8
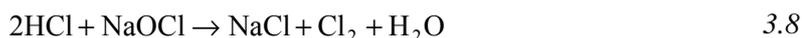
Following acid dosing, the brine is passed through three dechlorinators in which the dissolved chlorine is displaced by an air stream blown through the dechlorinators (physical dechlorination). The displaced chlorine gas is routed to the sodium hypochlorite synthesis plant. The pH of the brine leaving the primary dechlorination stage is corrected through the addition of caustic soda (18% m/m NaOH).

A residual quantity of dissolved chlorine remains in the brine stream following physical dechlorination. This is removed by chemical (secondary) dechlorination. Chemical dechlorination involves the addition of excess sodium bisulphite (10% m/m NaHSO₃) to the brine. The chlorine is destroyed via the following reaction:

$$Cl_2 + 3NaOH + NaHSO_3 \rightarrow Na_2SO_4 + 2NaCl + 2H_2O \qquad \textit{3.9}$$
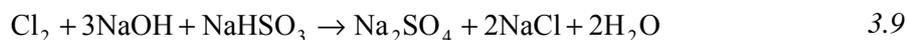
The build-up of sulphate in the circuit is controlled via the brine purge. The depleted brine is cooled and returned to the resaturator.

Cation-Exchange Regeneration

The cation-exchange regeneration sequence comprises seven stages: Brine Displacement, Backwash, Acid Regeneration, Acid Rinse, Caustic Regeneration, Caustic Rinse and Brine Replacement. During the Brine Displacement stage, brine is displaced from the cation-exchange resin bed using demineralised water. The Backwash stage sees the resin bed being flushed with demineralised water in the opposite direction to the brine flow. A weak hydrochloric acid solution (7% m/m HCl) is used for the Acid Regeneration stage. During this stage, the cation-exchange resin is converted from the divalent cation form to the hydrogen form:

$$MX_2 + 2HCl \rightarrow 2HX + MCl_2 \qquad \textit{3.10}$$

where HX is the hydrogen form of the cation-exchange resin. The hydrochloric acid hold-up from the Acid Regeneration stage is displaced from the resin bed using demineralised water (Acid Displacement stage). A weak caustic soda solution (4% m/m NaOH) is used in the Caustic Regeneration stage to convert the cation-exchange resin back to the sodium form:

$$HX + NaOH \rightarrow NaX + H_2O \qquad \textit{3.11}$$

The caustic soda hold-up from the Caustic Regeneration stage is displaced from the resin bed using demineralised water (Caustic Displacement). The regeneration sequence is completed by the replacement of brine in the resin bed (Brine Replacement). Effluent from the cation-exchange regeneration sequence is sent to an acid pit where partial neutralisation of the hydrochloric acid effluent by the caustic soda effluent occurs, prior to the effluent being discharged to the effluent treatment facility.

Chlorine Processing

The chlorine gas stream emerges from the electrolyser at an elevated temperature (~87 °C) and in a saturated state. The majority of this water condenses out of the chlorine gas stream in the chlorine cooler with the residual quantity being removed by concentrated sulphuric acid drying. The condensate from the chlorine cooler, which contains a quantity of dissolved chlorine, is

blended with the depleted brine stream prior to the primary dechlorination stage while the dry chlorine is either used within the complex or sent to storage.

Hydrogen Processing

The hydrogen gas stream leaves the electrolyser at an elevated temperature (~89 °C) and in a saturated state. Most of the water is removed via condensation as the hydrogen stream is cooled in the hydrogen cooler. Hydrogen gas leaving the cooler is either used internally within the complex, bottled for sale or cooled further in the hydrogen chiller for export to the hydrogen peroxide plant located on the Umbogintwini Industrial Site.

Caustic Evaporation

Caustic soda leaves the electrolyser at a strength of approximately 32% m/m NaOH. The concentration is increased to saleable strength (50% m/m NaOH) in the dual-effect caustic evaporation plant. Steam condensate and process condensate from the evaporators is recycled to the brine resaturator.

3.1.2.2 *The Hydrochloric Acid Synthesis Plant*

The hydrochloric acid synthesis plant comprises two hydrochloric acid synthesis units, each consisting of a burner and an absorption section. Chlorine gas is burnt in excess hydrogen gas in the burner to produce hydrogen chloride gas:

$$H_2 + Cl_2 \rightarrow 2HCl \qquad\qquad 3.12$$

The hydrogen chloride gas and unreacted gases rise into the absorption section of the unit where the hydrogen chloride is absorbed in demineralised water to produce hydrochloric acid. This is drawn off from the unit. The remaining gas stream is passed to a scrubber where a weak caustic soda solution removes any residual hydrogen chloride and chlorine gas prior to the gas stream being vented to the atmosphere.

3.1.2.3 *The Sodium Hypochlorite Synthesis Plant*

While sodium hypochlorite is produced for sale, the sodium hypochlorite synthesis plant has the added function of being a reliable sink for any excess chlorine present within the various process systems of the complex. All waste chlorine from the brine circuit and the chlorine processing system is sent to the sodium hypochlorite synthesis plant where it is reacted, together with a make-up chlorine stream, with dilute caustic soda (22% m/m NaOH) according to:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O \qquad\qquad 3.13$$
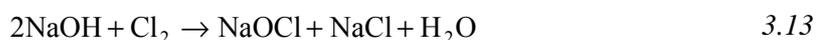
The sodium hypochlorite synthesis plant consists of five primary absorption towers, three of which are on-line at any given time. The dilute caustic soda is circulated over the absorption towers where it reacts with the chlorine. The batch is withdrawn from the towers when the sodium hypochlorite has reached the required strength (~17.5% m/m NaOCl).

3.1.2.4 *The Hydecat Destruction Plant*

With some of the sodium hypochlorite production being forced to absorb excess chlorine from the various process systems of the complex, the quantity of sodium hypochlorite produced sometimes exceeds the saleable demand. In such situations, or when the quality of sodium hypochlorite is off-specification, the waste sodium hypochlorite must be disposed of through the effluent treatment facility. Before disposal however, chlorine-releasing species must be destroyed so as to prevent downstream releases. This is done by processing the waste sodium hypochlorite in the Hydecat destruction plant. Waste sodium hypochlorite is diluted with Umbogintwini River water and preheated by direct steam injection. The dilute sodium hypochlorite (4% m/m NaOCl) is passed over a nickel-based catalyst which destroys the hypochlorite species, resulting in the evolution of oxygen:

$$2\text{NaOCl} \rightarrow 2\text{NaCl} + \text{O}_2 \qquad\qquad 3.14$$

The effluent produced by the Hydecat destruction plant, a weak brine solution with trace quantities of dissolved chlorine and nickel, is sent to the effluent treatment facility.

3.1.2.5 *The Demineralisation Plant*

The demineralisation plant provides a steady supply of high purity water to the various process systems within the chlor-alkali complex. The plant consists of a cation-exchange resin bed and an anion-exchange resin bed arranged in series. The raw water feed to the plant comprises an equal-ratio blend of Umgeni Water (municipal supply) and water from the Umbogintwini River.

During the normal ion-exchange cycle of operation, cations are removed from the influent water in the cation-exchange bed and the cation-exchange resin is converted from the hydrogen form to the cation form according to the reaction:

$$\text{M}^+ + \text{HX} \rightarrow \text{MX} + \text{H}^+ \qquad\qquad 3.15$$

where MX is the cation form of the cation-exchange resin. Anions are removed from the influent water in the anion-exchange bed and the anion-exchange resin is converted from the hydroxide form to the anion form according to the reaction:

$$\text{A}^- + \text{XOH} \rightarrow \text{XA} + \text{OH}^- \qquad\qquad 3.16$$

where A^- is an anion and XOH and XA are the anion-exchange resin in the hydroxide and anion forms respectively. These reactions proceed until the exchange capacities of the ion-exchange resins have been reached. Regeneration of the demineralisation plant takes place every 16 h.

The regeneration sequence comprises five stages: Pre-Inject, Regenerant Inject, Regenerant Displacement, Fast Rinse and Quality Rinse. The Pre-Inject stage establishes a flow of demineralised water through the elution ducts. During the Regenerant Inject stage, dilute caustic soda (~4% m/m NaOH) is used to convert the anion-exchange resin from the anion form to the hydroxide form and dilute hydrochloric acid (~4% m/m HCl) is used to convert the cation-exchange resin from the cation form to the hydrogen form. Demineralised water is used to displace the hydrochloric acid and caustic soda hold-ups from the cation-exchange and anion-exchange beds respectively during the Regenerant Displacement stage. Two rinse stages complete the regeneration sequence: a Fast Rinse stage, using raw water, and a Quality Rinse stage, using demineralised water. All effluent from the various stages, except that of the Quality Rinse stage which is recycled, is sent to the effluent treatment facility.

3.1.2.6 *Miscellaneous Operations*

Miscellaneous operations include those activities within the chlor-alkali complex that do not necessarily fall into the process systems described previously. These activities include: cooling circuits, pump seals, plant washdown, cylinder and drum pressure testing and cleaning, effluent pH correction and steam desuperheating.

Cooling Circuits

The complex has four cooling circuits: the Linde, the Sulzer, the Liquid Chlorine (LC) and the Membrane Cell (MBC). The Linde and Sulzer cooling circuits are associated with the liquefaction of chlorine while the LC cooling circuit meets the cooling requirements associated with the use of the liquefied chlorine. The MBC cooling circuit satisfies the cooling requirements of the brine circuit. All the cooling towers use water from the Umbogintwini River as make-up; the blowdown is sent to the effluent treatment facility.

Pump Seals

Demineralised water is used to maintain the seal on several pumps within the complex. This water is sent to the effluent treatment facility.

Plant Washdown

The plant is washed down once a week using Umbogintwini River water. This water is drained to the effluent treatment facility.

Cylinder and Drum Pressure Testing and Cleaning

The empty gas cylinders and drums are cleaned using steam and pressure tested using Umbogintwini River water. Effluent from these activities is sent to the effluent treatment facility.

Effluent pH Correction

The effluent treatment facility is owned and managed by Umbogintwini Operational Services (UOS) which serves the industrial site as a whole. Excess hydrochloric acid present in the effluent must be neutralised prior to the effluent leaving the Sasol Polymers site and this is done through the addition of concentrated caustic soda (~32% m/m NaOH) at a point near the boundary of the complex.

Steam Desuperheating

Steam is supplied to the Sasol Polymers site by UOS in a superheated form. This steam is desuperheated by direct injection of demineralised water.

3.2 A REVIEW OF THE INITIAL STUDY AT SASOL POLYMERS

The set of processes described in **Section 3.1.2** represents a subset of those considered by Gardner in the initial Water Pinch Analysis study carried out at the chlor-alkali complex (Gardner, 1999). In addition to these operations, the complex included a Cereclor plant, a trichloroethylene-producing solvents plant, an acetylene generation plant and a vinyl chloroacetate plant. These operations were decommissioned during the course of the initial study and are therefore not included in this follow-up study.

In his analysis of the chlor-alkali system, Gardner noted that the reactivity of the HCl and NaOH species present in the system introduces a further dimension to the problem of water minimisation. With these species being much more valuable than water, their recovery is desirable. As such, the situation presented by the chlor-alkali complex is one in which the optimal design strategy relative to cost may not coincide with the one featuring the lowest water consumption and effluent generation. Gardner noted further the presence of a number of dilution-type operations on the complex. These operations involve the dilution of either concentrated caustic soda or concentrated hydrochloric acid with freshwater such that a stream or intermediate strength is produced. Gardner identified three utilisation patterns for the diluted reagent stream: it could be used to manufacture a product, it could be sent directly to the effluent treatment facility, or it could be sent to an operation in which the reagent is completely or partially used, with the resulting stream being sent to the effluent treatment facility. As such, the reagent-containing streams from the last two situations could be

recovered and used for dilution purposes instead of freshwater; this practice would result in savings in concentrated reagent and water-use, and effluent production.

Concentrated reagents usually have to be purchased by an industrial complex; in this case they are produced on-site. Dilution operations are required to bring the concentrated reagent from its supply strength to the various lower strengths required on the plant, as determined by process requirements. As such, the flow and concentration of the stream produced by the dilution operation are fixed and a specific quantity of water and a specific quantity of concentrated reagent are needed to meet these requirements. From a different perspective, the outlet stream of the dilution operation may be characterised by a fixed mass-load of reagent species and a fixed flowrate, both of which are set by process requirements. In meeting these requirements, there is a total flow balance and a reagent species balance for the dilution operation which must be satisfied. Where only freshwater and concentrated reagent are used to produce the dilute stream, the flow balance includes contributions from both the freshwater and concentrated reagent streams; the reagent species balance is however satisfied completely by the contribution from the concentrated reagent source. Where a reagent-containing effluent is used for dilution purposes, the reagent species balance includes contributions from both the effluent and concentrated reagent sources. As a consequence of the effluent's contribution to this species balance, a smaller quantity of concentrated reagent is required by the operation. Hence, in order to meet the fixed flowrate requirement of the dilution operation, the amount of dilution water, supplied either by the reagent-containing effluent or freshwater, must increase.

In summary, the use of a reagent-containing effluent for dilution purposes corresponds to a decrease in the amount of concentrated reagent required by the dilution operation, but an increase in the amount of dilution water required. Diluting the concentrated reagent using only freshwater corresponds to the smallest amount of dilution water but the greatest amount of concentrated reagent. Conversely, the smallest requirement for the concentrated reagent occurs when the concentration of the reagent species in the reagent-containing effluent is at the concentration produced by the dilution operation. The amount of dilution water required by the operation is therefore dependent on the concentration of reagent species present in the diluting stream.

In identifying an approach to targeting the optimal water and reagent use strategy for the chlor-alkali complex, Gardner noted that most of the operations within the complex do not fall into the mass-exchange category. For this reason, Gardner did not consider the use of the Wang and Smith approach (Wang and Smith, 1994) or that proposed by El-Halwagi and Manousiouthakis (1989). The reactivity issue, associated with the presence of HCl and NaOH, was circumvented by classifying the complex's streams and operations into three distinct groups: one for HCl-tolerant streams and operations, one for NaOH-tolerant streams and operations, and a third group for the remaining streams and operations. As it was pointed out, this decomposition strategy inadvertently resulted in the problem being approached from a single contaminant perspective. The decomposition was however justified by Gardner who noted that the HCl concentration limit for an NaOH-tolerant operation would be zero and vice versa. A further simplification was made by excluding those streams for which the flowrate

fell below a particular threshold value from the analysis. This simplification was justified by Gardner on the basis that it would be economically impractical to recover these streams.

The approach adopted by Gardner in addressing the problem presented by the chlor-alkali complex was a modification of the Two-Composite methodology proposed by Buehner and Rossiter (1996) and Dhole et al. (1996), and involved the construction of source and demand composite curves with the reagent species as the contaminant. This modification was required because the reagent demands are characterised by a fixed concentration requirement instead of a maximum concentration limit. In representing the demands, the assumption was made that the dilution operation was able to accept water of a quality up to the concentration of the reagent species produced by that operation; this assumption was aimed at promoting the recovery of reagent-containing effluents, which in turn represents the most effective total cost strategy. Given that the water demand for an operation depends on the concentration of the reagent species present in the dilution water, the targeting procedure became iterative. Table 3.1 presents a summary of the results obtained by Gardner.

Table 3.1. *Summary of the results obtained from the initial Water Pinch Analysis study carried out at the Sasol Polymers chlor-alkali complex at Umbogintwini. (Gardner, 1999)*

	Original Flow [kg/h]	New Flow [kg/h]	Percentage Saving [%]
NaOH Network			
Water	4 785	0	100
Effluent	5 667	1 971	65
Caustic Soda (100% m/m NaOH)	1 180	1 146	2.9
HCl Network			
Water	763	0	100
Effluent	5 467	4 114	25
Hydrochloric Acid (31% m/m HCl)	5 963	5 723	4.2
Non-NaOH/HCl Network			
Water	9 034	4 061	55
Effluent	11 047	6 074	45
Overall Savings			
Water	14 582	4 061	72
Effluent	22 181	12 159	45
Caustic Soda (100% m/m NaOH)	1 180	1 146	2.9
Hydrochloric Acid (31% m/m HCl)	5 963	5 723	4.2

In concluding his study, Gardner noted the suitability of the modified Two-Composite methodology to the simultaneous targeting of water and reagent use. It was however recommended that theory pertaining to the targeting and design of networks involving reactive species be developed. In a further recommendation, Gardner pointed out that the modified Two-Composite methodology developed for the study required extension to take into account the multiple contaminant nature of the problem. Detailed economic evaluation in terms of capital expenditure and a more comprehensive feasibility analysis of the proposed networks were recommended prior to the implementation of the proposed water and reagent use strategy.

3.3 THE APPLICABILITY OF EXISTING TECHNIQUES AND TOOLS TO THE CHLOR-ALKALI SYSTEM

Results from the initial Water Pinch Analysis study (Gardner, 1999) showed that there was significant potential for savings to be effected on the chlor-alkali complex through the reuse and recovery of water and reagents. However, the approach adopted by Gardner resulted in the problem being considered from a single contaminant perspective; as such the optimality and even the feasibility of the proposed network configurations could not be guaranteed from the multiple contaminant perspective. Thus, with a number of changes also having taken place on the complex in terms of the closure of certain plants, the follow-up study was proposed with the intention of optimising water-use from the multiple contaminant perspective.

As evidenced by Gardner's study, the chlor-alkali complex does not correspond to the typical situation associated with the application of Water Pinch Analysis. Existing Water Pinch Analysis tools and the theory from which they developed rely on the assumption that a clear distinction can be made between so-called water streams and process streams. With this distinction in place, only the water-side of the problem is considered in the Pinch Analysis with the process-side being represented implicitly. As will however be illustrated by the following discussion, it is not easy to distinguish between process streams and water streams in the chlor-alkali complex.

Consider the brine circuit presented in Figure 3.2 in **Section 3.1.2.1**. The most sensitive region of this circuit is the electrolyser for which there exists a range of strict concentration limits on the various species in the brine stream, in particular calcium and magnesium cations. Calcium and magnesium cations enter the brine circuit alongside the sodium chloride in the raw salt and are removed from the circuit via the series of operations which precede the electrolyser. The major portion of the calcium and magnesium load is removed via the precipitation stage. During this stage, sodium carbonate is used to precipitate the calcium as calcium carbonate and caustic soda is used to precipitate magnesium as magnesium hydroxide, both of which are subsequently removed via clarification.

Precipitation of calcium carbonate and magnesium hydroxide are controlled by their associated solubility products. Thus, using the precipitation of calcium carbonate for the purposes of discussion, to achieve a desired residual calcium cation concentration in the stream leaving the precipitator requires an adjustment to the dose of sodium carbonate. The amount of sodium carbonate required is further dependent on the concentration of calcium cations entering the precipitator. Hence, if the calcium cation load entering the precipitator was to increase through the reuse of water or the recovery of reagent, an additional amount of sodium carbonate would be needed to produce the required residual concentration in the outlet stream. Thus a balance must be struck between the savings achieved through increased reuse of water and reagents and the penalties incurred through the need to remove additional contaminant loads from the system.

This situation recurs in a number of other operations within the brine circuit, including the ion-exchanger which precedes the electrolyser. The ion-exchanger reduces the concentration of calcium and magnesium cations to a level acceptable to the electrolyser. Given that the exchange capacity of the ion-exchange resin is fixed, an increase in the concentration of calcium and magnesium cations entering the ion-exchanger will require an increase in the regeneration frequency and thus the associated cost. A similar situation occurs in the hypochlorite destruction step following the electrolyser. Here, the amount of hydrochloric acid required to destroy the hypochlorite present in the depleted brine stream emerging from the electrolyser is dependent on the concentration of hypochlorite present in the depleted brine. Chemical dechlorination involves the same situation once more with the amount of sodium bisulphite added to destroy the residual chlorine being dependent on the concentration of chlorine present in the brine stream. Thus, as with the case of the precipitators, a compromise must be reached between the savings due to increased water-reuse and reagent recovery and the penalties incurred due to the additional effort required to remove the added contaminant load from the system.

A further aspect of the above operations is the transformation of species via chemical reaction. In each case, a reagent species is reacted with a contaminant species to effect the removal or elimination of that contaminant species from the system. This corresponds to the appearance and disappearance of species from the system. Individual species are therefore not independently conserved as is the case with the non-reacting systems considered by Water Pinch Analysis tools and theory. Chemical reactions do not only occur between reagent species and contaminant species either. A range of by-products are generated via chemical reaction in the electrolyser alongside the caustic soda, chlorine and hydrogen products. These species are contaminants which must either be eliminated from the system or their concentration controlled within the system. Further operations in which chemical reactions take place include the hydrochloric acid synthesis plant, the sodium hypochlorite synthesis plant, the Hydecat destruction plant, the demineralisation plant and the effluent pH correction stage. In addition, the operating cost of the demineralisation plant and the effluent pH correction stage is dependent on the contaminant load entering the operation.

In light of the preceding discussion, it is possible to identify three key aspects to the problem presented by the chlor-alkali complex which make the application of current Water Pinch Analysis theory to the situation difficult. These aspects are:

- The interactions that exist between process streams and water streams. These interactions make it difficult to distinguish between the two;

- The presence of multiple resources, in this case reagents and raw materials, in addition to water. These resources carry species which have an economic value to the system and are therefore desirable; and

- The chemical reactions taking place between the various species in the system.

While these aspects are noted, it is not to say that it is impossible to use Water Pinch Analysis to identify water-use strategies for the chlor-alkali complex. Current Water Pinch Analysis theory however relies on the distinction being made between process streams and water streams and excludes desirable and reactive species. Given that these aspects cannot be included, the water-use strategies that Water Pinch Analysis is able to identify will not be as efficient as those identified using an approach which does take these aspects into consideration. As a quantification of this, the use of standard Water Pinch Analysis tools to the problem is considered in **Appendix B**.

In light of the identified limitations in the existing Water Pinch Analysis theory however, an attempt has been made to provide a formal description of the approach required by the problem presented by the chlor-alkali complex (Gianadda et al., 2000, 2002a,b). In particular, such a description should provide a theoretical framework which incorporates both the new approach and the existing theory such that it remains applicable to problems presently handled by the existing methodology. In dealing with the first of the highlighted aspects, the concepts of *Utility-Water Pinch Analysis* and *Process-Water Pinch Analysis* are introduced (Gianadda et al., 2000; 2002a,b). Utility-Water Pinch Analysis is used to describe the existing theory which relies on the process system being segregated into a set of process streams and a set of water streams. The *utility* part of the definition comes from the observation that in such systems, water functions primarily as a utility, often involved in the removal of contaminant mass-loads from process streams. Process-Water Pinch Analysis is used to describe the situations where a clear distinction between process streams and water streams cannot be drawn. As such, the *process* part of the definition refers to the interactions between the process-side and the water-side of the system. It is further important to note that Process-Water Pinch Analysis is a superset of Utility-Water Pinch Analysis.

While the conceptual definitions of Utility-Water Pinch Analysis and Process-Water Pinch Analysis provide a theoretical framework for the first of the identified aspects of the problem, they do not include multiple resources. It is also debatable whether the task can still be considered purely as a Water Pinch Analysis problem. While the presented approach does draw on ideas for which the foundation lies within Water Pinch Analysis theory, in terms of the

formulation of the problem and the interpretation of results, efficient reagent and raw material use are not specific objectives of Water Pinch Analysis. For this reason, the concept of *Combined Water and Materials Pinch Analysis* is introduced for systems involving water and other resources. It is noted that these resources refer to raw materials and reagents and not energy, and hence the use of the word *material* in the conceptual definition. As such this approach seeks to determine the cost optimal strategy for water, raw materials and reagents. Given that reagents are included under this banner of *materials* the approach includes a means of handling the chemical reactions that accompany the use of these materials

3.4 CONCLUDING REMARKS

In terms of the objectives of this study, **Chapter 3** has provided an assessment of the suitability of the current Water Pinch Analysis theory and tools to the problem presented by the chlor-alkali complex. Three aspects of the problem which make the application of the current theory difficult were identified. These aspects are that there is no clear distinction between process streams and water streams in the process system, that multiple resources and desirable species are involved in the problem, and that some of the species present in the system are reactive. In addressing these issues, the conceptual definitions of Utility-Water Pinch Analysis and Process-Water Pinch Analysis were introduced; these definitions provide a framework for dealing with systems involving significant interactions between process streams and water streams. These definitions however do not include efficient reagent and raw material use as objectives; the concept of Combined Water and Materials Pinch Analysis was introduced as a result. With reagents being included in the category of *materials*, the handling of chemical reactions is included in this approach.

3.5 CHAPTER REFERENCES

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4

METHODOLOGY

The analysis of the problem presented by the chlor-alkali complex has highlighted the need for an approach which is able to consider water and material use simultaneously. This chapter develops the methodology for Combined Water and Materials Pinch Analysis. Section 4.1 presents the general problem statement for Combined Water and Materials Pinch Analysis while Section 4.2 considers the general approach to conducting a Combined Water and Materials Pinch Analysis study. Section 4.3 considers the formulation of the mathematical model for Combined Water and Materials Pinch Analysis and Section 4.4 considers this model in the context of the chlor-alkali complex. The formulated model consists of a superstructure, which represents the flows between sources and sinks in the system, and a number of process modules, which describe the performance of the individual process operations of the system; only the superstructure formulation is considered in Section 4.3. The process modules are made-up of combinations of four basic building blocks, namely mixing, flow separation, component separation and reaction; Section 4.5 presents the mathematical models for these building blocks. Finally, Section 4.6 presents some concluding remarks on this chapter as it relates to the objectives of this study.

4.1 PROBLEM STATEMENT FOR COMBINED WATER AND MATERIALS PINCH ANALYSIS.

The general problem statement for Combined Water and Materials Pinch Analysis may be presented as follows:

The process system is characterised by a set of process operations which convert the raw materials to the desired products at the desired production level. Within this process system, a number of demands for water, reagent and raw materials are present, each of which may be characterised by specific quantity and/or quality requirements which are established by the process operations. These demands must be satisfied using sources of water, reagent or raw material which are either available within the process system or supplied externally. Each external source, whether it be water, reagent or raw material, is characterised by a composition profile of contaminants and other species, a cost associated with its supply and possibly a finite availability limit. Each source within the process system is similarly characterised by a

composition profile of contaminants and other species and a finite availability limit, both of which are dependent on the functioning of the various process operations within the process system; these sources may also have a cost associated with their use. The process operations do not conform to any one particular model and may have any number of associated sources and demands. In addition, the various species present in the system may or may not be chemically reactive. Finally, the process system is characterised by certain effluent discharge limits, whether they be flowrate or composition based, which must be satisfied. As such, a number of different treatment operations, each with an associated cost which may be volume and/or load dependent, are available such that these discharge limits are satisfied. The task at hand is then to satisfy the various demands within the process system together with the effluent discharge requirements at the lowest overall cost.

The problem statement may be extended to include other considerations such as imposed and forbidden matches, safety, controllability and plant geography. The overall cost may comprise only operating costs or the total annualised investment cost. The assumption is made that energy and pressure effects are not significant. The assumption is also made that the process operations are functioning optimally for the current water allocation, that is, the optimisation problem conforms to the planning problem rather than the design problem as described by Takama et al. (1980a). As usual, this problem considers the system at steady-state.

4.2 THE GENERAL APPROACH TO COMBINED WATER AND MATERIAL PINCH ANALYSIS.

While there exists a significant amount of literature on the design of water systems, little guidance is provided on how exactly an investigation should proceed. In addition, much of the literature tends to deal with relatively small and self-contained problems which appear somewhat abstract in comparison to large and existing process systems. This section outlines a structured approach to conducting a Combined Water and Materials Pinch Analysis investigation on an existing process system. It should be noted that the approach is of a general nature and equally applicable to the typical Water Pinch Analysis investigation.

Consideration of the approach to conducting a Water Pinch Analysis investigation is given by Mann and Liu (1999), who consider a general strategy to the problem, and Tainsh and co-workers (Tainsh and Rudman, 1999; Baetens and Tainsh, 2000), who outline a strategy around the use of the software suite WaterTarget™ (Linnhoff March Limited, 2001). Gianadda et al. (2000) outline the stages of a Water Pinch Analysis investigation for the retrofit of an existing plant as follows:

1 Data acquisition and reconciliation

2 Pinch problem formulation

3 Optimisation

4 Review of the practical/economic feasibility of results with new constraints being imposed where necessary – this stage may involve different levels of simulation

5 Return to Stage 3

6 Implementation

As is the case with any optimisation problem, it is necessary to represent the various options available such that they can be analysed and the best set of options identified. In the context of the water network retrofit problem, it is the existing network configuration from which this set of possibilities arises. **Stage 1** in the Combined Water and Materials Pinch Analysis investigation therefore involves the collection of data from the plant. In practice, this exercise takes place over a period of time during which operating conditions typically change. Given that a steady-state frame of reference is required for Pinch Analysis, data reconciliation is carried out to produce a consistent representation of the process system. It is from this representation that the appropriate data are extracted and used to formulate the Pinch Analysis problem (**Stage 2**), which is subsequently optimised in the following stage (**Stage 3**). It should be noted that given the inherent complexity of the process system, the problem considered in the optimisation stage is a simplified representation of the process system. As such, it comprises only those factors which are likely to limit water-reuse (Wang and Smith, 1995) and in this case reagent and raw material recovery. Instead of representing the various process operations using rigorous process models, simplified models are derived from the existing plant records and used to approximate the behaviour of these operations. The solution obtained from the optimisation stage is analysed, possibly through various levels of simulation, to determine the economic or practical feasibility of the proposed network configuration with additional constraints being applied to the problem as and where necessary (**Stage 4**). This simulation step is recommended to take account of those factors not considered by the optimisation step but which may prove decisive in the end. Such factors may have been omitted from the optimisation step due to an initial assumption that they were unimportant or due to difficulties in representing these factors, for example, pH. Having imposed additional constraints, the updated problem is solved and the solution analysed once more (**Stage 5**). This iterative cycle continues until a suitable network configuration is established, which is then implemented (**Stage 6**).

While this strategy is outlined as a series of distinct steps, it is important to note that these steps are interrelated, particularly in the case of the first three steps (Gianadda, 2002). As such, it is the capabilities of the optimisation tools or methods which determine the level of detail required in data collection and strongly influence the way in which the problem is formulated. Despite the importance of these steps however, little guidance on these areas is provided by the literature. Some consideration is given to the area of data extraction for Pinch Analysis (Linnhoff and Akinradewo, 1999) but in the context of energy integration. Some of the principles outlined however remain applicable to the water and material minimisation situation

and in particular the importance of identifying features inherent in the existing network configuration. As such, these features may not be globally optimal and the problem should be formulated in such a way that they are not carried over to succeeding network configurations, unless deemed appropriate by the optimisation.

The area of problem formulation in the context of water minimisation is however not given any consideration by the literature outside the scope of this study. This step involves the postulation of the superstructure of possibilities from the existing network configuration. Gianadda (2000) outlines a heuristic-based approach for transforming the existing process network into a superstructure which is then optimised. Apart from assisting with the formulation of the Pinch Analysis problem, the procedure, which is perhaps more appropriately described as a conceptual guideline, provides insight into what data are required by the Pinch Analysis and thus aids the data gathering stage. The success of the approach lies in a shift in how the process system is viewed. Instead of viewing it as a sequence of process units, the system is perceived as a collection of conceptual operations, sources and demands. These conceptual operations, demands and sources may correspond to single unit operations, parts of individual unit operations or groups of unit operations. These are established by taking note of which areas of the process system are able to change during the course of the optimisation step. Here it is noted that regardless of changes proposed by the optimisation step, the process system still needs to produce the desired products from the available raw materials and at the required production level.

4.3 MODEL FORMULATION FOR COMBINED WATER AND MATERIALS PINCH ANALYSIS

This section presents a general mathematical model for Combined Water and Materials Pinch Analysis. This model involves the representation of the various options as a superstructure, as is the usual practice with this type of problem. Before presenting the model however, consideration must be given to the inclusion of process operations not conforming to one particular structure (**Section 4.3.1**) and the presence of desirable and reactive species in the system; these issues are dealt with in **Section 4.3.2** and **Section 4.3.3** respectively. **Section 4.3.4** presents the general model for the Combined Water and Materials Pinch Analysis problem while the representation of desirable species in the model is revisited in **Section 4.3.5**. The approach used to solve the problem is outlined in **Section 4.3.6**.

4.3.1 The Modular Approach Concept

The superstructure for the water and materials minimisation problem represents the set of inter-process flows between the various process operations within the process system and the flows to and from the external sinks and sources respectively. The typical superstructure encountered in the literature on water minimisation comprises only a single type of process operation (Takama et al., 1980a,b; Doyle and Smith, 1997; Alva-Argáez et al., 1998;

Alva-Argáez, 1999; Mann and Liu, 1999; Benkő et al., 2000; Dericks et al., 2001; Bagajewicz and Savelski, 2001), that is, the fixed contaminant mass-load addition model considered by Wang and Smith (1994). The majority of operations encountered on the chlor-alkali complex however do not conform to one particular type of unit model. Apart from not being able to describe the different operations according to a single performance characteristic such as mass transfer, the operations do not have a common physical structure in terms of the number of associated inlets and outlets. In formulating the superstructure for the model, it remains desirable that the model framework be of a sufficiently general nature such that all process operations can be integrated efficiently and easily. As such, the overall framework of the superstructure should be independent of the types of process operations considered such that the approach can readily be applied to any range of different process systems comprising any range of different process operations. This is accomplished by formulating the superstructure in such a way that it represents the set of all flows from any and all sources (supplies) within the process system to any and all sinks (demands) within the process system. The models for the individual process operations are then incorporated as modules within this framework and hence the conceptual idea of the modular approach. The superstructure is thus described as follows:

- Every sink, whether its destination is external or within the process system, is preceded by a conceptual mixer.
- Every source, whether its origin is external or within the process system, is followed by a conceptual splitter.

Figure 4.1 illustrates the superstructure framework for the modular approach. The incorporation of three process modules is illustrated in Figure 4.2.
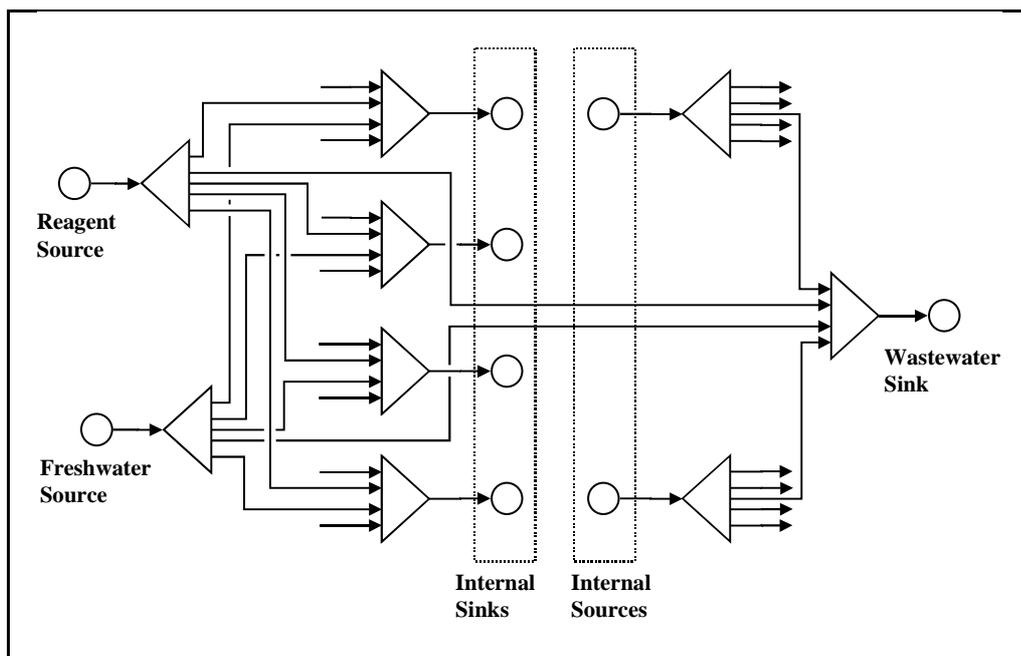
Figure 4.1. *An example of the superstructure framework for the modular approach to Combined Water and Materials Pinch Analysis.*
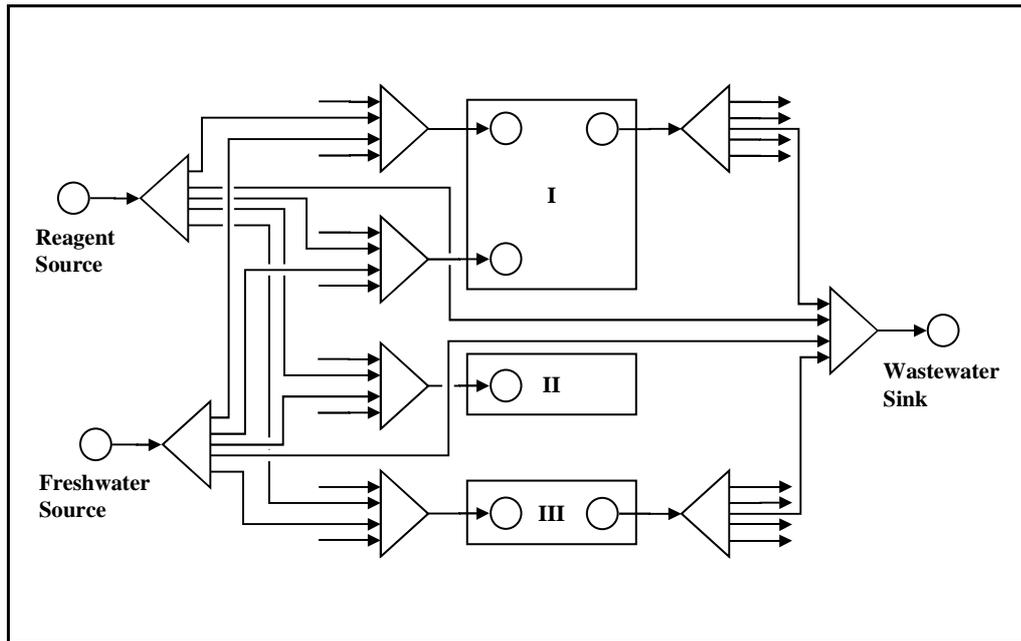
Figure 4.2. *An example of the superstructure framework for the modular approach to Combined Water and Materials Pinch Analysis with three process modules included in the superstructure.*

4.3.2 Considerations for Desirable Species

As has already been established, the species population associated with the chlor-alkali system includes both desirable and undesirable species. Demands for water, reagents or raw materials are usually characterised by a species concentration profile. This profile comprises maximum limits or constraints for the concentrations of the undesirable species which take the form:

$$C_k \leq C^{MAX}_k \qquad\qquad 4.1$$

where C_k is the concentration of species k associated with the flow into the demand and C^{MAX}_k is the maximum concentration of species k permitted by the demand. Where a demand is associated with the entry of raw materials or reagents into the system, the concentration profile includes other constraints that ensure that the raw materials or reagents enter the system at the appropriate concentrations. This calls for equality constraints of the form.

$$C_k = C^{REQ}_k \qquad\qquad 4.2$$

where C^{REQ}_k is the concentration of species k required by the demand. Given the presence of both desirable and undesirable species in the system, it is necessary to include both types of constraints in the Combined Water and Materials Pinch Analysis model.

4.3.3 Considerations for Reactive Species

As noted previously, a desirable mathematical characteristic of the optimisation model is that it be as simple as possible such that it is readily solved by the optimisation algorithm. In keeping with this concept, it is a common characteristic of all the models on water minimisation presented in the literature that they involve species which blend linearly. While this assumption is appropriate for many non-interacting species, reactive species do not blend linearly in practice. The reactivity of species is however related to a more general problem of incorporating the aquatic chemistry of the species present in the chlor-alkali system into the model.

In practice, dissolved salts, acids and bases become dissociated to varying degrees into anions and cations in water. As such, a single salt dissolved in water will dissociate to produce a range of aquatic species, the distribution ratios of which depend on complex species equilibria. For example, Na_2SO_4 dissociates such that a solution of Na_2SO_4 contains the species H^+, OH^-, Na^+, SO_4^{2-}, HSO_4^- and $NaSO_4^-$ at equilibrium, as can be verified from elementary aquatic chemistry (Snoeyink and Jenkins, 1980). When streams, which may possibly contain different species, are mixed together at stream junctions, the proportions of these species change according to a new set of equilibria. The implications of these phenomena are that the streams do not blend linearly. Instead, the appearance and disappearance of species is described by complicated nonlinear equilibrium relationships. A question thus arises as to how these species should be represented in the optimisation model. Certainly, using the more complicated nonlinear equilibrium relationships in the optimisation model adds further complexity to a problem which is already difficult to solve and may render it near impossible to solve.

One way around this problem is to ignore the speciation effects in the optimisation model. Referring once more to the aqueous solution of Na_2SO_4, it is certain that if a particular mass of Na_2SO_4 is dissolved in water, then the water will contain that mass of Na_2SO_4 regardless of how it becomes speciated. The entire speciated population may thus be represented by the mass-load concentration of Na_2SO_4. If another solution containing a certain quantity of NaCl is mixed with this Na_2SO_4 containing solution, then the combined solution will contain the same amount of Na_2SO_4 and NaCl as the component solutions. Effectively, this re-establishes the linear blending requirement at stream junctions. Issues of speciation are then addressed outside of the optimisation step and during the simulation stage.

Of course the characteristics of the species involved are of significance and must be considered when this modelling assumption is applied. For example, should a solution of NaOH be mixed with a solution of HCl the resulting solution will not contain the equivalent amounts of NaOH and HCl as the component solutions (Equation 4.3). Instead, the resulting solution will contain a quantity of NaCl (speciated as Na^+ and Cl^-) equivalent to the reaction between the species NaOH and HCl, and a quantity of either NaOH or HCl, depending on which of the two species is the limiting reactant. Given that the product of this reaction has different properties to the reactants, and that these differences are significant to the system, it is necessary to represent

certain species transformations in the model. Species transformations of this kind must however be represented in some way such that the linear blending requirement is satisfied in the model.

$$HCl + NaOH \rightarrow NaCl + H_2O \rightarrow Na^+ + Cl^- + H_2O \qquad\qquad 4.3$$
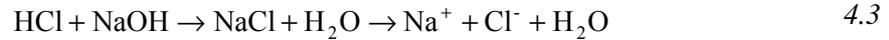
4.3.4 A General Model for Combined Water and Materials Pinch Analysis

The mathematical model for Combined Water and Materials Pinch Analysis problem is presented below. No knowledge of the physical structure of the process modules is assumed in this formulation. The outlet flows and concentrations from these process modules are however assumed to be functions of the inlet flows and concentrations. Consideration of the elements which make-up these process modules is provided in **Section 4.5** and will not be considered here. The actual structure of the various process modules of the chlor-alkali complex is presented in **Chapter 5**. The model described here therefore corresponds to a description of the superstructure into which the process modules are incorporated and includes the objective function for the problem. It is noted that in this formulation of the superstructure, sources are differentiated into two categories - those with constant species concentration profiles (primary sources) and those for which the species concentration profile is variable (secondary sources). External sources are primary sources while sources generated within the process system may be either primary or secondary. Primary sources are designated with a PSRC superscript while secondary sources are designated with a SSRC superscript; sinks are designated with a SNK superscript.

The model is thus presented as follows:

Sets

$$H = \left\{ h \,|\, h \text{ is a primary source} \right\}$$

$$I = \left\{ i \,|\, i \text{ is a secondary source} \right\}$$

$$J = \left\{ j \,|\, j \text{ is a sink} \right\}$$

$$K = \left\{ k \,|\, k \text{ is an aqueous species} \right\}$$

Parameters

Concentration Parameters:

$C^{MAX}_{j,k}$ Maximum concentration for species k associated with sink j. Species k is considered undesirable at sink j

$C^{REQ}_{j,k}$ Required concentration for species k associated with sink j
                                                 Species k is considered desirable at sink j

$C^{PSRC}_{h,k}$ Concentration of species k in primary source h

Cost Parameters:

CST^{PSRC}_{h} Cost associated with the use of primary source h

CST^{SSRC}_{i} Cost associated with the use of secondary source i

CST^{SNK}_{j} Cost associated with the discharge of flow into sink j

Connection Existence Parameters:

$L_{i,j}$ Lower limit for the mass flow between secondary source i and
                                                 sink j - determines whether a connection is feasible or not

$U_{i,j}$ Upper limit for the mass flow between secondary source i and
                                                 sink j - determines whether a connection is feasible or not

<u>Continuous Variables</u>

Flow Variables:

F^{PSRC}_{h} Total mass flow from primary source h

F^{SSRC}_{i} Total mass flow from secondary source i

F^{SNK}_{j} Total mass flow to sink j

$F^{PSRCSNK}_{h,j}$ Mass flow from primary source h to sink j

$F^{SSRCSNK}_{i,j}$ Mass flow from secondary source i to sink j

Concentration Variables:

$C^{SSRC}_{i,k}$ Concentration of species k associated with secondary source i

$C^{SNK}_{j,k}$ Concentration of species k associated with sink j

Objective Variable:

TC   Operating cost

Mixed-Integer Variables

$Z_{i,j}$ Variable corresponding to the existence or non-existence of a mass flow between secondary source i and sink j

Constraints

Mass-Balance Constraints around Splitters:

$$F^{PSRC}_h = \sum_j F^{PSRCSNK}_{h,j} \qquad\qquad 4.4$$

$$F^{SSRC}_i = \sum_j F^{SSRCSNK}_{i,j} \qquad\qquad 4.5$$

Mass-Balance Constraints around Mixers:

$$F^{SNK}_j = \sum_h F^{PSRCSNK}_{h,j} + \sum_i F^{SSRCSNK}_{i,j} \qquad\qquad 4.6$$

$$F^{SNK}_j \cdot C^{SNK}_{j,k} = \sum_h F^{PSRCSNK}_{h,j} \cdot C^{PSRC}_{h,k} + \sum_i F^{SSRCSNK}_{i,j} \cdot C^{SSRC}_{i,k} \qquad\qquad 4.7$$

Concentration Constraints - Undesirable Species:

$$C^{SNK}_{j,k} \leq C^{MAX}_{j,k} \qquad\qquad 4.8$$

Concentration Constraints - Desirable Species:

$$C^{SNK}_{j,k} = C^{REQ}_{j,k} \qquad\qquad 4.9$$

Mixed-Integer Constraints:

$$F^{SSRCSNK}_{i,j} - L_{i,j} \cdot Z_{i,j} \geq 0 \qquad\qquad 4.10$$

$$F^{SSRCSNK}_{i,j} - U_{i,j} \cdot Z_{i,j} \leq 0 \qquad\qquad 4.11$$

Objective Function:

$$TC = \sum_h CST^{PSRC}_h \cdot F^{PSRC}_h + \sum_i CST^{SSRC}_i \cdot F^{SSRC}_i + \sum_j CST^{SNK}_j \cdot F^{SNK}_j \qquad\qquad 4.12$$

Equations 4.4 to 4.11 represent a mixed-integer nonlinear programming (MINLP) formulation of the superstructure into which the models for the process modules are incorporated[1]. Before considering a modification to the way in which desirable species are handled in this model, the following comments are made regarding the above model formulation.

- Where the models reported in the literature involve volumetric flows, the above model formulation uses mass flows. Models in the literature only involve water and the assumption is made that all streams are dilute; the densities of all streams are thus equivalent to water and volumetric flows blend linearly at stream junctions. Reagent and raw material species are however required at higher concentrations and the densities of these streams are different to that of water. In order to satisfy the linear blending requirement at stream junctions, it is necessary that streams be represented in terms of mass flows.

- Equations 4.10 and 4.11 (Grossmann, 1996; Alva-Argáez, 1999) together constrain the value of $F^{SSRCSNK}_{i,j}$ to the range between the lower limit $L_{i,j}$ and the upper limit $U_{i,j}$. As such, a connection between secondary source i and sink j will only be possible if the value of $F^{SSRCSNK}_{i,j}$ falls within the feasible range. Outside of this range, the value of $F^{SSRCSNK}_{i,j}$ will be forced to zero by the binary variable $Z_{i,j}$. These constraints may be used in the Combined Water and Materials Pinch Analysis problem to eliminate unrealistically small material flowrates between sources and sinks from the final solution. Equations 4.10 and 4.11 further need to be present in the problem formulation if other mixed-integer constraints are to be included in the model. Such constraints may be formulated to limit the number of streams which combine at a mixer or the number of streams branching at a splitter. Mixed-integer variable constraints may also be used to eliminate direct and indirect recycles. Consideration of these constraints is provided by Alva-Argáez (1999) while Grossmann (1996) overviews the transformation of logical decisions into mathematical relationships.

- The objective function described by Equation 4.12 includes only operating costs. Capital costs could be included by the addition of terms to Equation 4.12 together with a suitable annualisation factor as presented by Alva-Argáez (1999).

4.3.5 Considerations for Desirable Species - Revisited

The representation of desirable species in the superstructure model described by Equations 4.4 to 4.11 is inconvenient since the desirability of a particular species at one point in the system does not mean that it is universally desirable. For example, the species HCl is desirable where

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[1] *Equation 4.12 is the objective function of the optimisation problem and is not considered part of the superstructure.*

the demand requires hydrochloric acid, but undesirable where the demand requires caustic soda. The desirability of a species is thus specific to a demand and not to the species. Demands may further have concentration constraints for both desirable and undesirable species associated with them. Including concentration constraints in the above formulation would thus require each demand to be addressed separately. In addressing these demands an assessment would have to be made regarding the desirability of each species at that demand, with the incorporation of the appropriate concentration constraint, that is, either Equation 4.8 or Equation 4.9. This procedure is tedious.

In overcoming this problem, the observation is made that all raw materials and reagents species have an inherent economic value to the system. It should thus be possible to represent the desirable species in terms of an inequality constraint rather than an equality constraint. This takes the form:

$$C_k \geq C^{MIN}_k \qquad\qquad 4.15$$

where C^{MIN}_k is the minimum concentration of species k permitted by the demand. Given the higher economic value of the reagents and raw materials relative to water for the chlor-alkali system and that the objective function seeks to minimise the overall cost, the equality takes effect. Hence, the minimum value on these constraints coincides with the specific concentration at which the reagent or raw material is required by the demand, that is:

$$C^{MIN}_k = C^{REQ}_k \qquad\qquad 4.16$$

Formulating the concentration constraints for desirable species as inequalities has the advantage that it makes the representation of the model more concise. In particular, by the introduction of a scalar multiple, the same constraint can be used to represent both desirable and undesirable species concentration requirements of demands. This constraint takes the form:

$$M \cdot C_k \leq M \cdot C^{LIM}_k \qquad\qquad 4.17$$

where M is a scalar multiple which takes values of 1 if the species is undesirable and -1 if the species is desirable and C^{LIM}_k is the limiting (maximum or minimum) concentration of species k permitted by the demand.

The final model for the superstructure sees the combination of Equation 4.7 and Equation 4.17 as follows:

$$MM_{j,k} \cdot (\sum_h F^{PSRCSNK}_{h,j} \cdot (C^{LIM}_{j,k} - C^{PSRC}_{h,k}) + \sum_i F^{SSRCSNK}_{i,j} \cdot (C^{LIM}_{j,k} - C^{SSRC}_{i,k})) \geq 0$$

$$4.18$$

where $MM_{j,k}$ is a matrix of parameters describing the desirability of species k at demand j and $C^{LIM}_{j,k}$ is the limiting concentration (maximum or minimum) for species k at demand j. As previously, $MM_{j,k}$ takes a value of 1 if species k is undesirable at demand j and a value of -1 if species k is desirable at demand j. The more concise representation of the superstructure now involves Equations 4.4 to 4.6, 4.10 to 4.11 and 4.18.

It should be noted that while Equation 4.18 does provide a single equation for both desirable and undesirable species, there are situations where the equality must be enforced for desirable species. Such occasions occur when the desirable species enters an operation from which it emerges having been only partially used. In these situations, the possibility of cascaded-use of the reagent exists, that is, from one operation to another operation, and it may be necessary to include an additional concentration constraint in the model such that the reagent is delivered to the demand at the required concentration and not one higher than required.

4.3.6 Solution Approach

Equations 4.4 to 4.6, 4.10 to 4.12, and 4.18 represent an MINLP formulation of the Combined Water and Materials Pinch Analysis problem. The general approach adopted by this research was to solve the problem as a relaxed mixed-integer nonlinear programming (RMINLP) problem. The RMINLP problem resembles the MINLP problem except that the solution algorithm treats the mixed-integer variables as continuous variables. Should it be necessary to enforce the mixed-integer constraints, then the MINLP model can be solved using the solution from the RMINLP problem as a starting point[1]. Regardless of the strategy for handling the mixed-integer constraints, the model is nonlinear and non-convex and, as a result, the determination of the global optimum is inherently difficult. The nonlinearities in the superstructure arise from the bilinear product terms of species concentration and flowrate. Being non-convex, these terms result in the presence of a number of local optima in the search space. It is these local optima which make the search for the global optimum difficult.

While it is not possible to identify the location of the global optimum with certainty, there are certain measures which may be taken such that there is an increased probability that the local solution the optimisation algorithm converges to will be coincidental to the global optimum. These measures include efforts which bring about a reduction in the problem size, a reduction in the number of variables taking zero as a value, and a reduction in the number of non-convexities in the model, all of which are reported to produce difficulties for the optimisation algorithm (Grossmann, 1996). The probability of locating the global optimum is also increased by supplying different starting points to the optimisation algorithm (Edgar et al., 2001).

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[1] *As it turned out, the mixed-integer component of the model was not used for this project; the model could thus have been solved purely as an NLP. In the interests of providing a general formulation of the problem however, the mixed-integer component of the model was kept and the model solved as an RMINLP.*

4.4 COMBINED WATER AND MATERIALS PINCH ANALYSIS FOR THE CHLOR-ALKALI COMPLEX

Having presented the general mathematical model for Combined Water and Materials Pinch Analysis in **Section 4.3**, attention now shifts to the application of this general model to the chlor-alkali complex. In particular, consideration is given to implementing some of the measures which bring about an improvement in the ability of the optimisation algorithm to locate the global optimum (**Section 4.4.1**). Once these measures have been considered, attention is given to the use of standard optimisation software for the problem in **Section 4.4.2**; the specific optimisation software used for this research is GAMS (General Algebraic Modelling System). **Section 4.4.3** considers a feature of GAMS which is used to reduce the size of the optimisation problem while **Section 4.4.4** considers the model architecture for the Combined Water and Materials Pinch Analysis problem as formulated in GAMS.

4.4.1 Measures for Improving the Solvability of the Combined Water and Materials Pinch Analysis Problem

The superstructure described by Equations 4.4 to 4.6, 4.10, 4.11 and 4.18 assumes that material may flow from any source within the process system to any sink within the process system. The nature of the chlor-alkali process system is however one that does not allow flow from every source to every sink within the process system. For example, since the species HCl and NaOH cannot coexist within the same stream, no flow from a source containing the reagent species HCl should be sent to a demand requiring NaOH, firstly for economic reasons but more likely for operability reasons, and vice versa. As far as representing this situation within the model is concerned, two options exist. The first option sees the formulation of a superstructure that includes the possibility of flow from a source containing HCl to a demand requiring NaOH. To ensure that no flow from the HCl-containing source enters the NaOH demand, additional constraints are included in the model. These constraints either take the form of integer constraints which forbid the matches directly, or other constraints which set the value of the flows from sources containing the species HCl to demands requiring NaOH to zero. Species concentration constraints may also be used. These measures however introduce further complexity to the model and contribute to the number of variables which take values of zero. The second option involves the formulation of a superstructure which excludes the possibility of flow from a source containing HCl to a demand requiring NaOH from the outset. No additional constraints are required and the model is simplified accordingly. This measure reduces the size of the search space and thus improves the probability of locating the global optimum.

It has been noted previously that variables taking values of zero are problematic for the solution of the optimisation model. For the solution of the RMINLP problem, the optimisation algorithm CONOPT, a feasible path algorithm, is used (GAMS Development Corporation, 2001). Some insight into the functioning of feasible path algorithms is thus appropriate at this point.

The directional search procedure of a feasible path algorithm is based on the strategy of first finding an initial and feasible point, that is, one that satisfies all of the model constraints, and then using the derivatives of the objective function at this feasible point to determine the search direction that should be followed such that a better feasible point is found (GAMS Development Corporation, 2001). This new point is used in the succeeding search step. Given that the progress of the optimisation algorithm towards the optimal solution is via a series of feasible solutions, each one better than the previous, the whole procedure relies on the initial feasible solution and the derivatives at this point. In addition, given that non-convexities are present in the model, multiple local optima may be present within the search space and thus an initial point in the vicinity of the global optimal solution is more likely to converge to the globally optimal solution (GAMS Development Corporation, 2001). Initial values of zero are noted to be particularly problematic for nonlinear variables and especially if these appear in product terms. In such cases, the value of the initial derivative becomes zero which suggests, as far as the optimisation algorithm is concerned, that the objective function is independent of that variable.

The nature of the chlor-alkali system is such that several variables within the model take values of zero. In particular, because species like HCl and NaOH are unable to coexist in the same stream, the value of at least one of these concentrations must always be zero, in reality. In addition, these variables exist in the product terms of species concentration and flowrate in the species mass-balances (Equation 4.7); this is thus problematic for the solution of the Combined Water and Materials Pinch Analysis problem. Before introducing an approach which circumvents this difficulty however, there is a further issue to be considered.

One of the characteristics of the chlor-alkali system is that it contains species for which different orders of magnitude of concentration are significant. At the one end of the spectrum, calcium and magnesium Ca^{2+} and Mg^{2+} are contaminants for which concentrations of significance to the process system are of the order of parts per billion. However, concentrations of significance for species such as NaCl, HCl and NaOH are of the order of hundreds of grams per kilogram of solution, a difference of eight orders of magnitude[1] relative to the concentrations of Ca^{2+} and Mg^{2+}. The problem with this order of magnitude range is that the optimisation algorithms require the variables to be well-scaled such that they are able to function optimally. As such, it is recommended that all variables and derivatives have

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[1] *It should be noted at this juncture that this issue causes some difficulty in terms of the number of significant figures considered during the data reconciliation and optimisation steps. With species being linked via chemical reactions, it was considered appropriate from a calculations perspective to consider the entire order of magnitude range during data reconciliation and optimisation steps, even if this is considered inappropriate from a scientific perspective - see discussion in **Appendix A***

expected values within two orders of magnitude of unity for optimal performance of the optimisation algorithm (GAMS Development Corporation, 2001).

In dealing with the problems associated with the presence of species concentration variables taking values of zero and the scaling of these variables, the following linear transformation is proposed. Firstly the concentrations of all species are expressed as mass fractions and a value of 1 is added to each species concentration. The modified concentration scale therefore has the following properties:

- Values of 1 on the modified concentration scale represent a true concentration of zero.
- Values of 2 on the modified concentration scale represent a true concentration of unity, that is, pure substances.

The use of the modified concentration scale thus places all species concentration variables in the range of unity and reduces the number of variables taking zero as a value in the model. Being a linear transformation, the modelling requirement that the species blend linearly is maintained.

A number of additional points should be made regarding the above transformation.

- The mathematically rigorous approach to scaling the variables involves the use of a scaling factor which reduces the actual range spanned by the variables to the range [0,1]. This implies that a different scaling factor would be required for each species. Given that the species interact chemically, it would be necessary to include these scaling factors when the chemical reactions are taken into account. The above transformation, though not mathematically rigorous circumvents this problem.

- While the value of the concentration variables is in the range of unity, the final decimal places for Ca^{2+} and Mg^{2+} are significant. The tolerance on the optimisation algorithm must thus be set at an appropriate level to maintain this level of significance.

4.4.2 Modelling Tools - GAMS

It is common practice to use a computer-based approach for the solution of mathematical programming problems. Aside from the task of formulating the problem in a mathematical sense, some effort is required to convert the problem into a format which can be handled by the specific optimisation algorithm chosen to solve the problem, an activity which can prove time-consuming. Circumventing this step has been one of the primary motivations in the development of the software language GAMS (General Algebraic Modelling System). GAMS is a high-level language for the compact representation of large and complex optimisation problems (Brooke et al., 1998). A key feature of the language is that the model may be

described independently of the required solution algorithm. Thus, models are formulated using a consistent notation and within a common development environment, termed the Integrated Development Environment (IDE), which is independent of the nature of the problem, that is, whether the problem conforms to an LP, MILP, NLP or MINLP problem, and independent of the solution algorithm required to solve the problem. As new or improved solution algorithms become available in time, their application to established models can be carried out without the need to reformulate the problem. GAMS thus comprises two component parts - the first is the Integrated Development Environment in which the model is developed while the second part comprises the different optimisation algorithms which are called by GAMS according to the model type, that is, LP, NLP etc..

A further characteristic of the software is that the optimisation problem can be expressed independently of the data it uses (Brooke et al., 1998). This allows the size of the problem to be increased without affecting the complexity of the model's representation. Thus, the problem structure for the Combined Water and Materials Pinch Analysis problem is independent of the number of species considered and the number of process operations (sources and sinks) involved.

Despite the infinite number of optimisation problems that could be considered, all GAMS models have a common structure which is illustrated in Figure 4.3.

Sets	e.g. the set of species
Data Entry	Scalars Parameters (listed data) Tables (tabulated data)
Variables	Continuous & integer variables Objective variable Upper & lower bounds on variables
Initialisation	Initial values for variables such that equations are feasible
Equations	Equalities & inequalities describing the performance of the system Objective function
Model & Solve Statements	Selection of which equations to include in the model Selection of solution method

Figure 4.3. *Schematic diagram of the general structure of a GAMS model.*

Like any programming language, GAMS has different data classes and these correspond to sets, data entries, variables and equations. Sets constitute the simplest building blocks in the GAMS model and correspond directly to the indices in the algebraic representation of the model. Data constants are introduced into the GAMS model using one of the three data input structures, namely scalars, parameters and tables. Scalars are used for single datum entries while parameters correspond to lists of data; tables correspond to data presented in tabulated form. The third section of the GAMS model corresponds to the definition of the model variables, whether they be continuous or integer variables. The objective variable is declared within this section and upper and lower bounds on the different variables imposed. The model is initialised by providing a set of initial values for the variables such that all the model constraints, which are present in the body of equations which follows this initialisation section, become feasible. This body of equations includes both equalities and inequalities and describes the performance of the system under consideration. It is further within this body that the objective function is specified. The remaining part of the GAMS model involves the specification of which of the equations should be considered by the optimisation algorithm and which of the available optimisation algorithms should be called by GAMS to solve the problem.

4.4.3 A GAMS Feature used in Combined Water and Materials Pinch Analysis

It has been noted that the problem presented by Combined Water and Materials Pinch Analysis is difficult to solve and **Section 4.4.1** considered some of the measures which may be employed such that the probability of locating the global optimum is improved. This section considers how a feature in GAMS may be used for this purpose.

In **Section 4.4.1**, it was noted that the nature of the chlor-alkali process system was such that it does not allow flow from every source to every sink within the process system. As such, it was proposed that in formulating the superstructure for the problem, all matches between sources and sinks in the process system that are known to be inappropriate, be excluded from the superstructure from the outset.

In implementing this option, it is noted that one of the functions of the IDE is to transform the model from the standard compact notation of the IDE to the actual problem that is considered by the optimisation algorithm. As such, logical operators available within the IDE can be used to eliminate terms from the model as it is constructed for the optimisation algorithm, should certain criteria for term inclusion not be met. Hence, by the introduction of a connectivity matrix of ones and zeros, which correspond to the logical possibility of a connection between a particular source and a particular sink within the process system, inappropriate matches can be eliminated from the superstructure from the outset. The superstructure constructed by the IDE for the optimisation algorithm therefore comprises only those matches between the various sources and sinks which are realistic possibilities.

At this point, some clarification on the differences between these logical parameters and the mixed-integer variables already included in the problem formulation is appropriate. Both of these are associated with the existence or non-existence of a connection between a source and a sink. However the logical parameter corresponds to the decision, that a connection is feasible, being made at the problem formulation stage, while the mixed-integer variable corresponds to the decision being made during the course of the optimisation and by the optimisation algorithm.

As a further point on the use of the connectivity matrix in reducing the size of the optimisation problem, care should be exercised such that only those matches which are known to be inappropriate are excluded from the problem. If matches which could be feasible are excluded from the problem, the globally optimal water and material reuse strategy for the system under consideration might be overlooked. This consideration, that the global optimum is included amongst the set of possibilities represented in the optimisation model, is noted by Grossmann et al. (1999).

4.4.4 Combined Water and Materials Pinch Analysis - GAMS Model Architecture

The model formulated for Combined Water and Materials Pinch Analysis does broadly conform to the model structure shown schematically in Figure 4.3. However, as a result of applying the modular approach concept, there are distinct areas of the model which are associated with the establishment of the superstructure and other areas which are concerned with the specific process modules. As such, there are parameters, variables and constraints associated specifically with the superstructure and other parameters, variables and constraints associated with the process modules. In addition, the objective variable and objective function can be distinguished from the superstructure component and the process module component of the model.

As noted previously, the model is formulated as an MINLP problem and solved initially as an RMINLP problem. Structurally, it is possible to arrange the problem such that it is formulated as an NLP with the mixed-integer component of the problem confined to a specific area. Hence, if integer constraints are not a concern, the problem may be considered purely as an NLP problem - the mixed-integer component is thus optional.

Figure 4.4 illustrates the structure of the overall model and distinguishes between the areas of the model associated with the superstructure, the objective function and the different process modules. Figure 4.4 also shows the structure of an individual process module and how modules are incorporated in the model. The location of the optional mixed-integer component in the model is also indicated.
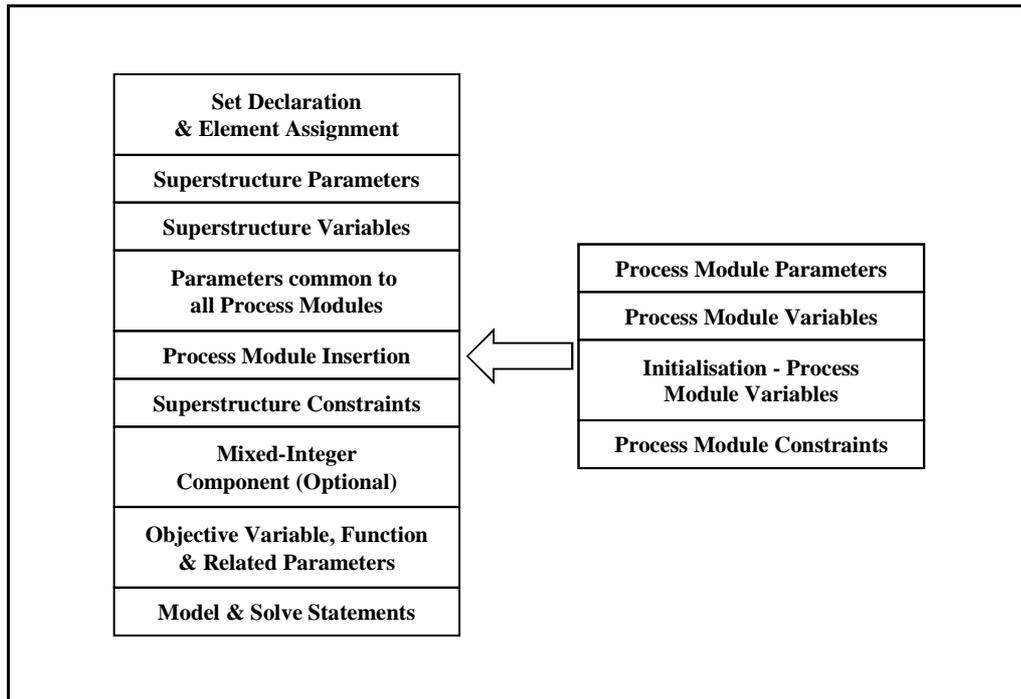
Figure 4.4. *Schematic diagram of the structure of the GAMS model for Combined Water and Materials Pinch Analysis with the various components of the model indicated and the structure of the process module illustrated.*

4.5 THE PROCESS MODULE COMPONENT

Process operations present in the process system are represented in the Combined Water and Materials Pinch Analysis problem as process modules. Where the superstructure represents the set of flows between the various sources and sinks within the process system, process modules provide the informational link between the different sinks and sources. Thus, taking the simple mass-load addition model as an example, the process module for this operation describes how a mass-load of contaminant is added to the water entering the operation (sink), such that the particular quantity and quality of effluent is produced by the operation (source).

One characteristic common to all process modules is that all cycles of operation of the equipment are represented in the model. Thus a process module representing an ion-exchange operation includes both the ion-exchange and regeneration cycles of operation together with the relationship between these two cycles. Where certain of these cycles of operation are noncontinuous, time averaged models are used.

Given that the process operations within the chlor-alkali complex are varied in terms of their physical structure and operating characteristics, the discussion of specific process modules is presented in **Chapter 5** which deals with the specific case studies of the chlor-alkali complex. However, each process module is made up of combinations of four basic building blocks,

namely mixing, flow separation, component separation and reaction, as shown in Figure 4.5. The mathematical models for these building block elements are considered in this section.
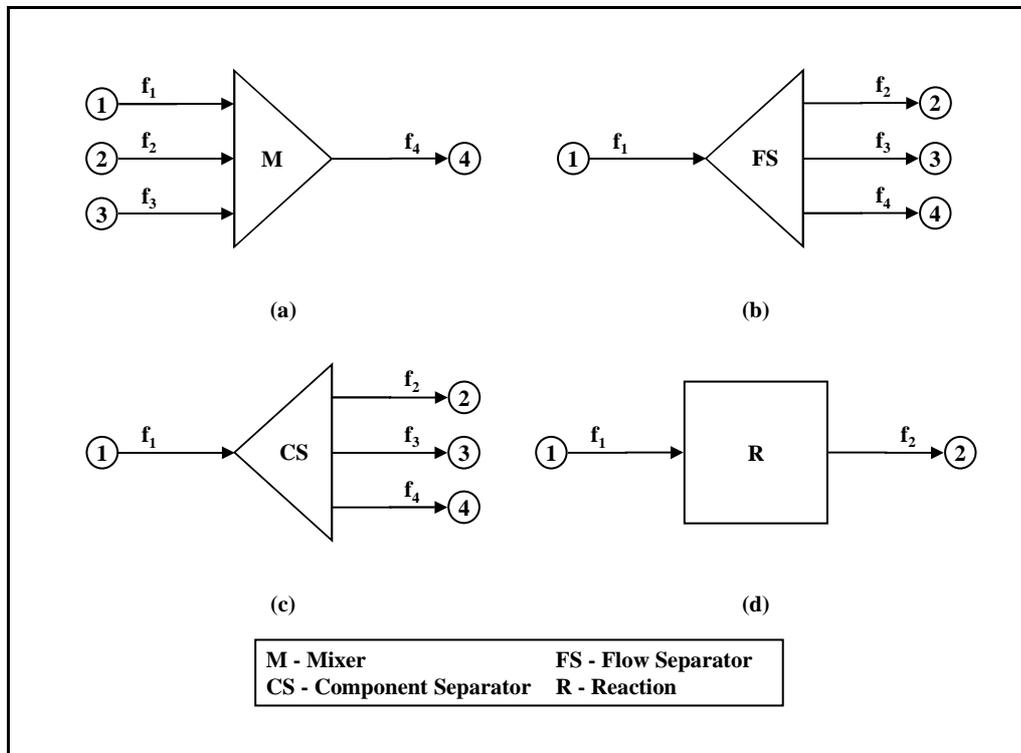
Figure 4.5. *Diagram of the basic building blocks used to assemble a process module in the Combined Water and Materials Pinch Analysis problem. (a) Mixer (M). (b) Flow separator (FS). (c) Component separator (CS). (d) Reaction (R).*

In general, parameters and variables specific to the different process modules are defined within each process module. Some of the variables common to the different building block elements of the process module include the mass flowrates and concentrations of species associated with the various streams of the building block elements. These are as follows:

f_n Mass flow associated with stream n in process module

$c_{n,k}$ Concentration of species k associated with stream n in process module

where n is a number assigned to a specific stream in the process module. The models for the various building blocks are presented below alongside any additional parameters and variables that are required. It is noted that species concentration is represented in these models in terms of the modified concentration scale.

Process Module Building Block - Mixing

The model for the mixing building block comprises a total mass-balance and component mass-balances for all the species. The model is presented as follows for the situation in which three streams combine to produce a fourth as shown in Figure 4.5a:

Mass-Balance Constraints for Mixer:

$$f_1 + f_2 + f_3 = f_4 \qquad\qquad\qquad 4.19$$

$$f_1 \cdot c_{1,k} + f_2 \cdot c_{2,k} + f_3 \cdot c_{3,k} = f_4 \cdot c_{4,k} \qquad\qquad\qquad 4.20$$

The mixing building block is used to model the deliberate combination of streams and the mass-load addition of species to streams within the process module.

Process Module Building Block - Flow Separation

The model for the flow separator comprises parameters representing the flow split ratios together with mass-balance constraints. For flow separators, the concentration of the various species is identical in each stream associated with the separator. The model is presented as follows for the situation in which one stream is divided into three as shown in Figure 4.5b:

Parameters:

S_n Flow split ratio associated with branch n from flow separator

Mass-Balance Constraints:

$$f_n = S_n \cdot f_1 \qquad n \in \{2;3;4\} \qquad\qquad 4.21$$

$$c_{n,k} = c_{1,k} \qquad n \in \{2;3;4\} \qquad\qquad 4.22$$

Clearly the sum of the split ratios must be unity; for the situation depicted in Figure 4.5b, this corresponds to:

$$\sum_{2}^{4} S_n = 1 \qquad\qquad\qquad 4.23$$

Equation 4.23 is not included as a constraint in the model but is observed when the model is formulated.

Flow separators are used to model a deliberate division of flow within the process module. In some situations, it is necessary to represent a fixed flow in one of the branches emerging from the flow separator. The inlet flow to the flow separator is however able to vary. In this

situation, it is not possible to represent the flow in the fixed flow branch via Equation 4.21 and a different formulation is required. For a flow separator with only two branches, that is, f_2 (fixed) and f_3, this takes the form:

$$f_2 = f_2{}^{REQ} \qquad\qquad 4.24$$

$$f_1 = f_2 + f_3 \qquad\qquad 4.25$$

where $f_2{}^{REQ}$ is the required flow in branch 2 from the flow separator. In many cases, the flow separator building block will involve a combination of the two models.

Process Module Building Block - Component Separation

Where the concentrations of the various species were identical in each stream associated with the flow separator, the concentrations of the various species may be different in the streams associated with a component separator. The model for the component separator comprises parameters representing the component split ratios together with mass-balance constraints. The model for the component separator is presented for the situation in which one stream is split into three as shown in Figure 4.5c:

Parameters:

$S_{n,k}$ Component split ratio associated with species k in branch n from component separator

Mass-Balance Constraints:

$$f_n = f_1 \cdot \sum_k S_{n,k} \cdot (c_{1,k} - 1) \qquad n \in \{2;3;4\} \qquad\qquad 4.26$$

$$f_n \cdot (c_{n,k} - 1) = S_{n,k} \cdot f_1 \cdot (c_{1,k} - 1) \qquad n \in \{2;3;4\} \qquad\qquad 4.27$$

Similarly, the sum of the component split ratios must be unity for each component. This corresponds to:

$$\sum_{n=2}^{n=4} S_{n,k} = 1 \qquad\qquad 4.28$$

Equation 4.28 is not included as a constraint in the model but is observed when the model is formulated.

Component separators are used to model separations taking place in the process module. For example, a component separator is used to model the removal of water via drying from a moist gaseous stream.

Process Module Building Block - Reaction

The reaction building block is used to represent chemical transformations of species in the process module. It comprises a single inlet and a single outlet as shown in Figure 4.5d. In addition to mass flow and concentration variables, the model comprises a variable corresponding to the molar extent of each reaction taking place within the block. Parameters are used to represent the stoichiometric coefficients of the species involved in the chemical reaction(s) associated with the reaction block. The stoichiometric coefficients of the reaction products are considered to be positive while those for the reactants are considered to be negative. Not all species are involved in the chemical reaction and two different species balances are required to represent non-reactive and reactive species. The model for a reaction block involving a single chemical reaction is presented below:

Parameters:

M_k Molar mass of species k

$N_{q,k}$ Stoichiometric coefficient for species k in reaction q
                                                          Greater than 0 for products of reaction q
                                                          Less than 0 for reactants of reaction q

Variables:

r_q Molar extent of reaction q in reaction block

Mass-Balance Constraints:

$$f_1 = f_2 \qquad\qquad\qquad \textit{4.30}$$

Non-Reacting Species:

$$c_{1,k} = c_{2,k} \qquad\qquad\qquad \textit{4.31}$$

Reacting Species:

$$f_1 \cdot (c_{1,k} - 1) + N_{q,k} \cdot M_k \cdot r_q = f_2 \cdot (c_{2,k} - 1) \qquad\qquad \textit{4.32}$$

There is one degree of freedom present in Equation 4.32. It is therefore necessary to specify either the molar extent of reaction taking place, r_q, or the concentration of a single (reference) species at the outlet of the reaction block, $c_{2,k}$. This reference species may correspond to a limiting reactant or one for which the concentration is known at the outlet of the reaction block. While the model presented above involves only a single chemical reaction, multiple reactions could be included. Each additional reaction associated with the reaction block however corresponds to an additional degree of freedom which must be satisfied.

Equations 4.31 and 4.32 could be combined into a single equation by introducing a logical matrix similar to the connectivity matrix used for reducing the size of the superstructure. This logical matrix would correspond to the logical involvement of a species in a particular reaction in the reaction block.

Having presented the different building blocks involved in the assembly of the process modules, it must be emphasised that each type of building block has a specific function, whether that be mixing, flow separation, component separation or reaction. As such, the model for the process module is constructed using only these single-functioned elements. **Chapter 5** provides a more detailed description of the process modules involved in the chlor-alkali system.

4.6 CONCLUDING REMARKS

In terms of the objectives of this study, **Chapter 4** has provided the mathematical framework for Combined Water and Materials Pinch Analysis. This methodology is able to deal with systems in which there are significant interactions between process streams and water streams, multiple resources, desirable and reactive species; this approach uses mathematical programming. The representation of the process system in the optimisation model comprises two parts, that is, the superstructure and the process modules. The superstructure represents the set of all possible flow configurations between sources and sinks within the process system. The process modules represent the various operations which make up the process system and are assembled from four basic building blocks, namely, mixing, flow separation, component separation and reaction. **Chapter 4** has presented the superstructure part of the optimisation model and the mathematical models for the basic building blocks which constitute the process modules; the specific process modules for the chlor-alkali complex are given consideration in **Chapter 5**.

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Having presented the general approach and mathematical formulation for Combined Water and Materials Pinch Analysis in Chapter 4, this chapter addresses the application of the methodology to the chlor-alkali complex. Section 5.1 defines the scope of the study at the chlor-alkali complex and identifies the species of significance to the system which are considered in the Pinch Analysis. The chlor-alkali complex is a large and complicated system and certain measures need to be taken to make the application of the methodology tractable; Section 5.2 presents the decomposition strategy used for handling the size and complexity of this problem. This decomposition strategy leads to the system being divided into a number of subsystems and Section 5.3 considers the modelling of the process modules associated with these subsystems and the optimisation of the subsystems in isolation from each other. Despite the decomposition strategy, the optimisation problems for the various subsystems remain complex; Section 5.4 presents some general points on the modelling and optimisation of these subsystems. Concluding remarks on this chapter, as it relates to the objectives of this study, are presented in Section 5.5.

5.1 THE SCOPE OF THE INVESTIGATION AT THE CHLOR-ALKALI COMPLEX

Before specific case studies related to the chlor-alkali complex can be considered, it is necessary to identify the scope of the investigation at the chlor-alkali complex. The system boundaries of the study are identified in **Section 5.1.1** while **Section 5.1.2** identifies the species of significance to the chlor-alkali system which are considered in the Pinch Analysis. **Section 5.1.3** presents a general note on the handling of assumptions made in this study.

5.1.1 System Boundaries

The system boundary for this investigation corresponds to the physical boundary of the chlor-alkali complex. The investigation does not consider the Umbogintwini Operational Services (UOS) effluent treatment facility which serves the industrial complex as a whole. The possibility of using recycled water from this facility is not considered. This assumption is justified since the combined effluents from a range of industries on the industrial site are

treated collectively in this centralised effluent treatment facility. As such, it is likely that the treated effluent will contain some quantity of material from another industry which prohibits its use in the chlor-alkali complex. More specifically, it is perhaps the risk associated with the use of this treated effluent that prohibits its recycle. The effluent treatment facility is thus treated as a terminal sink from a modelling point of view as proposed by Huang et al. (1999).

5.1.2 Species Selection

Table 5.1 presents a listing of the species of significance to the chlor-alkali system considered in this investigation. Included within this table is both a justification for the selection of the species and a categorisation of the species in terms of its associated desirability or undesirability. Some of these species are neither desirable nor undesirable, but are included since they are involved in some of the chemical reactions taking place on the complex. The inclusion of these species in the Pinch Analysis is not essential since they do not constrain the reuse of materials; their inclusion does however provide a more realistic representation of what is occurring in the system from a mass-balance perspective.

Table 5.1. *Species considered in the Combined Water and Materials Pinch Analysis investigation at the chlor-alkali complex with a justification for the representation of these species in the problem and a categorisation of the species in terms of their desirability.*

Species	Status	Justification for Selection
Ca^{2+}	Undesirable	Precipitates as hydroxide in electrolyser membranes
$CaCO_3$	Undesirable	A precipitate which can foul electrolyser membranes
Cl_2	Desirable	Product produced and raw material used by the complex
	Undesirable	Destroys cation-exchange resin in brine circuit
H_2	Desirable	Product produced and raw material used by the complex
HCl	Desirable	Product produced and reagent/raw material used by the complex
	Undesirable	Contaminant where caustic soda is required
H_2O	-	Involved in chemical reactions
Mg^{2+}	Undesirable	Precipitates as hydroxide in electrolyser membranes
$Mg(OH)_2$	Undesirable	A precipitate which can foul electrolyser membranes
$NaCl$	Desirable	Raw material used in the complex
	Undesirable	Contaminant in demineralised water production
$NaClO_3$	Undesirable	Damages cation-exchange resin in brine circuit
Na_2CO_3	Desirable	Used as a reagent to precipitate calcium in brine circuit
	Undesirable	Affects electrolyser membranes at high concentrations

cont.

Table 5.1. *cont.*

Species	Status	Justification for Selection
NaHSO$_3$	Desirable	Destroys Cl$_2$ in brine stream
	Undesirable	Converts to sulphate which is undesirable
NaOCl	Desirable	Product produced by the complex
	Undesirable	Cl$_2$ releasing species - problematic in brine circuit and effluent
NaOH	Desirable	Product produced and reagent/raw material used by the complex
	Undesirable	Contaminant where hydrochloric acid is required
Na$_2$SO$_4$	Undesirable	Diffuses through electrolyser membranes with some precipitation taking place
O$_2$	-	Product of chemical reactions
Insolubles	Undesirable	Fouling of equipment
TDS	Undesirable	Of significance in the cooling towers

In **Chapter 4** it was noted that salts dissolved in water exist as a group of dissociated species. However, with the exception of Ca^{2+}, Mg^{2+}, Insolubles and Total Dissolved Solids (TDS), all species listed in Table 5.1 are either salts or molecules. The species are considered in the Pinch Analysis in these particular states since the data available from the plant are presented in terms of these states. In the modelling, Ca^{2+} and Mg^{2+} are assumed to be associated with chloride anions. This is not an unreasonable assumption given that the primary source of these divalent cations is the raw salt. Ca^{2+} and Mg^{2+} are therefore represented as $CaCl_2$ and $MgCl_2$ respectively. The advantage of this assumption is that it allows the representation of some reactions to be neater which in turn simplifies the representation of these reactions in the optimisation model. Insolubles and TDS are composite species. Insolubles includes all insoluble matter but excludes $CaCO_3$ and $Mg(OH)_2$ which are treated separately. TDS is only of significance in the modelling of the cooling towers..

It should be noted that Table 5.1 does not represent an exhaustive list of species involved in the chlor-alkali complex. Other species of significance to the system are present but at concentrations which are not problematic to the system in its current configuration. Consideration of a species in the Pinch Analysis is only required if it is likely that a change proposed by the optimisation can result in a concentration change, which causes the species to become problematic or economically significant to the system. Hence, in deciding whether a species should be considered in the Pinch Analysis, some insight is required to identify all potential sources of that species. With regard to the range of species in the chlor-alkali system, two species of significance will be used to illustrate these ideas, namely nickel and biological growth.

Nickel enters the brine circuit as a trace component of the raw salt. The nickel load within the brine circuit is regulated by the cation-exchanger. Another source of nickel is the effluent emerging from the Hydecat destruction plant. This unit employs a nickel-based catalyst to destroy waste sodium hypochlorite and the effluent from the plant contains trace quantities of nickel cations. Since this effluent also contains significant quantities of sodium chloride, the possibility does exist that this effluent could be recovered to the brine circuit, with or without intermediate treatment. However, with nickel cations not being problematic in the existing configuration, no data are available regarding the performance of the various operations of the system with respect to nickel. Instead of gathering data for this species however, the assumption is made that the cation-exchanger would be able to deal with the slightly elevated levels of nickel in the brine circuit should the effluent be reused. Nickel is therefore not considered as a contaminant in the Pinch Analysis; its effects can however be quantified at the simulation stage and included subsequently if required.

Biological growth of micro-organisms is predominantly encountered on the complex within the cooling circuits, which are further considered to be the only, or at least dominant, sources of the contaminant. The reuse of water from the cooling circuits in other parts of the complex is considered risky because of these micro-organisms and is prohibited as a result. This contaminant is thus not included explicitly in the Pinch Analysis. This strategy for dealing with certain contaminants is similar to that proposed by Brouckaert et al. (2001).

5.1.3 A General Note on the Handling of Assumptions made in this Study

The nature of this type of study is one in which a large number of assumptions need to be made. The system under consideration is complex and a simplified representation is required for the optimisation; this simplified representation is assumed to approximate the performance of the system. Given the number of assumptions involved in the derivation of this representation, it is not considered practical to present a detailed analysis of each assumption; the more significant assumptions are however noted and discussed. A similar approach will be used in assessing the validity of the results obtained from the optimisation.

5.2 A DECOMPOSITION STRATEGY FOR THE CHLOR-ALKALI COMPLEX

The application of a decomposition strategy to a process system results in a number of smaller problems rather than one large problem. These smaller problems only involve parts of the process system and are therefore easier to solve. Decomposition strategies which divide the process system into a number of different zones have been proposed by Oleson and Polley (1996) as a means of dealing with plant geography in the design of water-reuse networks, and by Amidpour and Polley (1997) in the context of producing simpler designs for heat integration. In this investigation, the chlor-alkali complex has been divided into three subsystems, the classification of which has been based on the reuse potential of water from one

subsystem to another. Reuse opportunities for water are maximised within each subsystem before reuse opportunities are investigated in other subsystems. The subsystems identified are as follows:

- the demineralisation plant subsystem;

- the chemical production subsystem, which is made up of the brine circuit, the hydrogen and chlorine processing plants, the caustic evaporators, the hydrochloric acid synthesis plant, the sodium hypochlorite synthesis plant and the Hydecat destruction plant; and,

- the cooling circuit subsystem, which is made up of the various cooling towers and their associated cooling circuits located within the complex.

Aside from making it easier to handle the problem from the perspective of optimisation, there are issues of practicality in these divisions which add further justification to the strategy. In particular, water from the cooling circuit subsystem, which may have biological contaminants associated with it, is not allowed to enter the demineralisation plant subsystem or the chemical production subsystem. Similarly, effluent from the regeneration cycle of the demineralisation plant subsystem may not be reused in the chemical production subsystem or the cooling circuit subsystem.

Despite the compartmentalisation of the process system into subsystems, interactions between these divisions do exist. In particular, demineralised water from the demineralisation plant subsystem is required by the chemical production subsystem. Similarly, caustic soda and hydrochloric acid from the chemical production subsystem are required by the demineralisation plant subsystem. Thus in modelling the subsystems, it is necessary to incorporate these interactions. These interactions are however likely to change during the optimisation and these changes also need to be addressed.

With the subsystem approach to dealing with the chlor-alkali complex, water not reused internally within a subsystem is available for reuse in other subsystems. This interaction between the subsystems is handled by assigning a hierarchy to each subsystem with respect to the allocation of water resources from other subsystems. As has already been noted, water from the cooling circuit subsystem may not be reused in either of the other subsystems. Demineralised water from the demineralisation plant subsystem may be used in either of the other subsystems, though it may not be economically sensible to use the water in the cooling circuit subsystem. The chemical production subsystem however retains priority with regard to the use of demineralised water. Excess water from the chemical production subsystem may similarly be reused in either of the other subsystems. However, since the quality of the water entering the demineralisation plant subsystem holds greater implications with respect to cost compared to that for the cooling circuit subsystem, priority is assigned to reusing excess water from the chemical production subsystem in the demineralisation plant subsystem. Any of the water not accepted by the demineralisation plant subsystem is made available for use in the cooling circuit subsystem.

The existing interactions between the chemical production subsystem and the demineralisation plant subsystem require some analysis. The frequency of regeneration required by the demineralisation plant is subject to the demand for demineralised water by the chemical production subsystem. In addition, the frequency of regeneration may be decreased by the recovery of water from the chemical production subsystem to the demineralisation plant subsystem. The water from the chemical production subsystem is of a superior quality to the water currently used by the demineralisation plant, that is, municipal and river water. A lower regeneration frequency also implies reduced demands for hydrochloric acid and caustic soda from the chemical production subsystem. With smaller quantities of these reagents required within the complex, greater volumes are available for sale, leading to greater profits by the complex.

Figure 5.1 provides a schematic representation of the interactions between the various subsystems of the chlor-alkali complex. While certain elements of a conceptual strategy for dealing with the interactions have been outlined in the preceding discussion, a knowledge of the modelling of the three subsystems must be established before a more detailed description of the strategy is presented. Much of the remainder of this chapter is devoted to presenting this knowledge and further discussion of this issue is deferred until later.
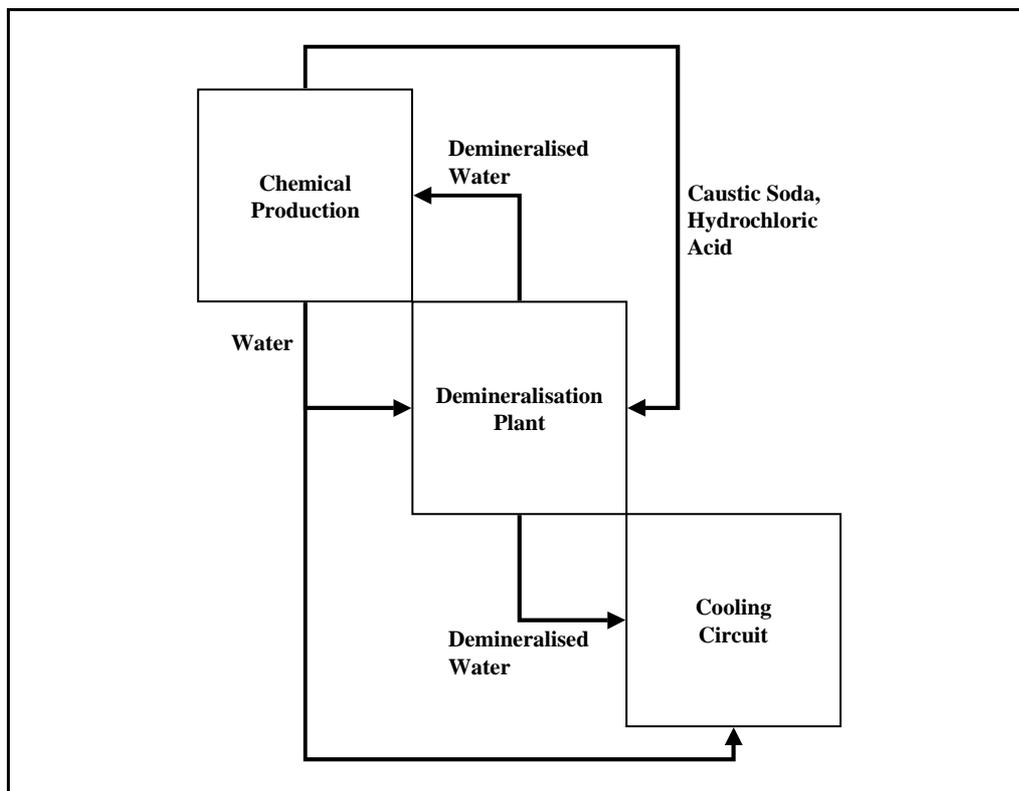
Figure 5.1. *Schematic diagram showing the interactions between the chemical production subsystem, the demineralisation plant subsystem and the cooling circuit subsystem.*

5.3 SUBSYSTEM MODELLING

Part of the decomposition strategy applied to the chlor-alkali complex involves the investigation of internal reuse opportunities within each of the identified subsystems. Only once the opportunities for reuse have been maximised within the individual subsystems are opportunities investigated in other subsystems. It is important to note that while the subsystems are considered independently, certain criteria affecting other subsystems, for example, production rates must be observed. The following section considers the modelling of each of the individual subsystems in isolation from each other. In particular, the different process modules which constitute the various subsystems are presented together with their integration into the superstructure framework presented in **Chapter 4**. In presenting these process modules, only the significant areas of the different models are highlighted. The full mathematical descriptions of the process modules may be found in the GAMS code which is presented on the **CD** accompanying this thesis. Given the analysis of the subsystems presented within this section, it is deemed appropriate to present some form of result produced by the solution of the optimisation model. A comparison is thus drawn between the water and material consumption and effluent production figures of the current scenario and the optimised scenario. Consideration of these results does however stop short of any further analysis since this issue is the focus of **Chapter 6**. The different subsystems are presented as follows: **Section 5.3.1** considers the demineralisation plant subsystem; **Section 5.3.2** considers the chemical production subsystem; and, **Section 5.3.3** considers the cooling circuit subsystem.

As a general strategy to the optimisation of the different subsystems, the initial set of concentration constraints imposed on the subsystem superstructures are derived from existing plant records. Relaxation of constraints is considered only in subsequent optimisation runs and only where appropriate.

5.3.1 The Demineralisation Plant Subsystem

Unlike the other subsystems, the demineralisation plant subsystem has only one process module, which is used to describe both the normal cycle of operation and the regeneration cycle of operation of the demineralisation plant. This section considers the optimisation of the demineralisation plant subsystem in isolation from the other subsystems. The demand for demineralised water within the chlor-alkali complex is therefore assumed to remain at the level at which it is currently required; this assumption will be relaxed when the different subsystems are integrated in **Chapter 6**. **Section 5.3.1.1** identifies the potential reuse opportunities associated with demineralisation plant and defines the set of possible matches considered in the optimisation. **Section 5.3.1.2** presents a description of the model for the demineralisation plant process module while **Section 5.3.1.3** presents the approach required for dealing with changes in the regeneration frequency associated with the demineralisation plant. Finally, **Section 5.3.1.4** presents the problem statement for the demineralisation plant subsystem.

5.3.1.1 Opportunities for Material Reuse in the Demineralisation Plant Subsystem

Figure 5.2 shows the different stages of the regeneration sequence, together with the effluents produced by each stage and the hold-up volumes at the conclusion of each stage. The positioning of the regeneration cycle relative to the normal cycle of operation is also indicated. The normal cycle of operation is represented in Figure 5.2a and 5.2h while the regeneration sequence is represented in Figure 5.2c to 5.2g. Figure 5.2b represents the changeover from the normal cycle of operation to the regeneration cycle.

The progress of fluid through the demineralisation plant during the regeneration sequence may be described as follows:

- **Changeover** (Figure 5.2b):

  When the changeover from the normal cycle of operation to the regeneration cycle is made, both the anion-exchange (A) and cation-exchange (C) resin beds contain raw water.

- **Pre-Inject Stage** (Figure 5.2c):

  The Pre-Inject stage introduces a small volume of demineralised water into each resin bed. This demineralised water displaces an equal volume of raw water from the bed. At the end of this stage, the resin bed contains raw water and the small volume of demineralised water introduced during the stage.

- **Regenerant Inject Stage** (Figure 5.2d):

  During the Regenerant Inject stage, hydrochloric acid, at the required concentration, is injected into the cation-exchange bed and caustic soda, at the required concentration, is injected into the anion-exchange bed. As the stage proceeds, water presently in the resin beds is displaced by the regenerants. Simultaneously, the cations are stripped from the cation-exchange resin and replaced by H^+ cations while the anions are stripped from the anion-exchange resin and replaced by OH^- anions. At the end of the stage, the resin bed volumes are occupied by the regenerants at the concentrations at which they were supplied to the stage. The effluent from this stage comprises a mixture of the raw water displaced from the resin beds, the regenerants that have passed through the resin beds and the ions eluted from the ion-exchange resins.
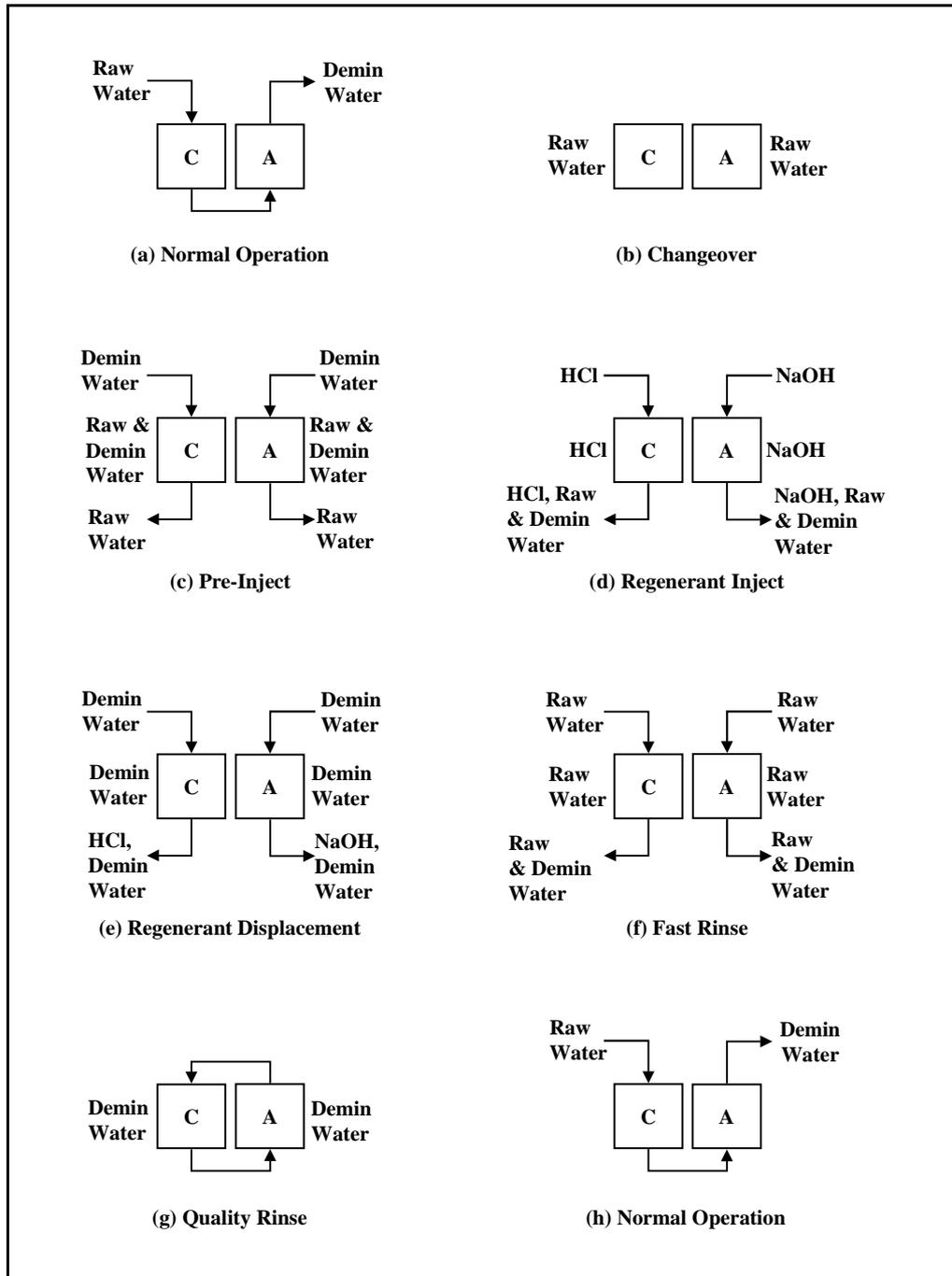
Figure 5.2. *Diagram illustrating the position of the regeneration sequence relative to the normal cycle of operation for the demineralisation plant. The various stages of the regeneration sequence are shown together with the hold-ups and effluents produced from each stage. (a) Normal cycle of operation. (b) The ion-exchange resin beds prior to the regeneration sequence commencing. (c) Pre-Inject stage. (d) Regenerant Inject stage. (e) Regenerant Displacement stage. (f) Fast Rinse stage. (g) Quality Rinse stage. (h) Normal cycle of operation.*

- **Regenerant Displacement Stage** (Figure 5.2e):

  During the Regenerant Displacement stage, demineralised water is used to displace the regenerant hold-ups from the Regenerant Inject stage. At the end of this stage, the resin beds are filled with demineralised water. The effluent from this stage is a weak hydrochloric acid solution from the cation-exchange bed and a weak caustic soda solution from the anion-exchange bed.

- The regeneration sequence is completed by two rinse stages, the Fast Rinse and the Quality Rinse:

  Fast Rinse Stage (Figure 5.2f):

  The Fast Rinse stage uses raw water. The demineralised water hold-up in the resin bed from the previous stage is displaced by this raw water and at the end of the stage the resin bed is filled with raw water. The effluent from the Fast Rinse stage is a mixture of the raw water that has passed through the resin beds and the demineralised water hold-up from the Regenerant Displacement stage.

  Quality Rinse Stage (Figure 5.2g):

  The Quality Rinse stage uses demineralised water. This water is recycled through the resin beds and after a period of time, the demineralisation plant returns to the normal cycle of operation (Figure 5.2h). No effluent is produced during this stage.

From the preceding description, four demands associated with the regeneration sequence of the demineralisation plant may be identified. These demands are for demineralised water, raw water, caustic soda and hydrochloric acid. Raw water is also required by the normal cycle of operation of the demineralisation plant. From a survey of the effluents arising from the regeneration cycle, the following potential reuse opportunities are identified:

- While the effluents from the Regenerant Inject stage were considered too contaminated for reuse, the effluents from the Displacement stage may be reused in subsequent regeneration cycles. From the cation-exchange bed, the effluent is a weak solution of hydrochloric acid and this could be used when the hydrochloric acid supply for the subsequent cycle is prepared. From the anion-exchange bed, the effluent is a weak solution of caustic soda and this could be used when the caustic soda supply for the subsequent cycle is prepared. Both reuse opportunities would result in savings in demineralised water, concentrated regenerant (reagent) and effluent treatment costs.

- Effluents from the Fast Rinse stage may be reused during the normal cycle of operation of the demineralisation plant. This effluent is a mixture of demineralised water and raw water. Its reuse would result in savings in raw water and effluent treatment costs.

Both of the above opportunities, if feasible, would further result in small reductions in the frequency of regeneration of the demineralisation plant. The reuse of the effluent (raw water) from the Pre-Inject stage is not considered a viable possibility since the quantity involved is small.

In investigating reuse opportunities for the effluents produced during the regeneration cycle, it should be noted that the assumption is made that all effluents are well mixed. In practice, there will be some profile which characterises the passage of the different fluids through the resin bed. Effluent would however need to be collected and stored if it is to be used in the succeeding regeneration cycle; sufficient mixing is thus assumed to take place during the collection of the effluent. In terms of the recovery of effluent from the Fast Rinse stage to the raw water feed to the demineralisation plant, the assumption that the effluent is well mixed is not actually necessary since the ionic load associated with the effluent is the same regardless of whether the effluent is well mixed or not.

From a modelling perspective, the superstructure concept implies that all flow emerging from a source in the superstructure must flow to a sink in the superstructure. Thus, all sources of effluent not reused directly within the demineralisation plant process module must be sent elsewhere and two terminal sinks are available for this purpose. The first sink is used for the storage of the demineralised water produced by the demineralisation plant while the second sink represents the effluent treatment facility. The connectivity matrix representing the logical possibility of connections between process sources and sinks for the demineralisation plant thus appears as shown in Table 5.2. All process sources may be sent to the effluent treatment facility.

Demands associated with the demineralisation plant process module not satisfied by the associated process sources must be satisfied by an external source. Two sources of raw water are available, namely Umgeni Water (municipal supply), for which an availability limit exists, and Umbogintwini River water, for which no availability limit exists. A single source of hydrochloric acid is available to meet the demands requiring hydrochloric acid, while three sources of caustic soda, each of differing strength, are available to meet the demands requiring caustic soda. These three sources correspond to the caustic soda produced by the electrolyser and the caustic soda withdrawn after the first and second effects of the dual-effect caustic evaporators. The connectivity matrix representing the logical possibility of connections between external sources and sinks for the demineralisation plant appears as shown in Table 5.3.

Table 5.2. *The connectivity matrix of possible matches between process sources and sinks for the demineralisation plant subsystem. An unshaded square corresponds to the logical possibility of a connection between a process source and a sink. Shaded squares correspond to the impossibility of a connection.*

(■ = shaded square / impossibility of a connection; blank = unshaded square / logical possibility of a connection)

Sources \ Sinks	Effluent Treatment Facility	Demineralised Water Storage	Raw Water Demand - Normal Operation	Raw Water Demand - Regeneration	Demineralised Water Demand - Regeneration	Caustic Soda Demand - Regeneration	Hydrochloric Acid Demand - Regeneration
Effluent - Cation Regeneration - Pre-Inject & Regenerant Inject Stage		■	■	■	■	■	■
Effluent - Cation Regeneration - Regenerant Displacement Stage		■	■	■	■	■	
Effluent - Cation Regeneration - Fast Rinse Stage		■		■	■	■	
Effluent - Anion Regeneration - Pre-inject & Regenerant Inject Stage		■	■	■	■	■	■
Effluent - Anion Regeneration - Regenerant Displacement Stage		■	■	■	■		■
Effluent - Anion Regeneration - Fast Rinse Stage		■		■	■	■	■
Demineralised Water			■	■			

Table 5.3. *The connectivity matrix of possible matches between external sources and sinks for the demineralisation plant subsystem. An unshaded square corresponds to the logical possibility of a connection between an external source and a sink. Shaded squares correspond to the impossibility of a connection.*

(■ = shaded square / impossibility of a connection; blank = unshaded square / logical possibility of a connection)

Sources \ Sinks	Effluent Treatment Facility	Demineralised Water Storage	Raw Water Demand - Normal Operation	Raw Water Demand - Regeneration	Demineralised Water Demand - Regeneration	Caustic Soda Demand - Regeneration	Hydrochloric Acid Demand - Regeneration
Umgeni Water (Municipal Supply)		■			■	■	■
Umbogintwini River Water		■			■	■	■
Hydrochloric Acid (31% m/m HCl)		■	■	■	■	■	
Caustic Soda (32% m/m NaOH)		■	■	■	■		■
Caustic Soda (38% m/m NaOH)		■	■	■	■		■
Caustic Soda (50% m/m NaOH)		■	■	■	■		■

The unshaded squares in Table 5.2 and Table 5.3 represent the total set of possible network configurations included in the optimisation problem for the demineralisation plant subsystem. It is from this set of configurations that the optimal network configuration will be selected.

5.3.1.2 *The Model for the Demineralisation Process Module*

Figure 5.3 illustrates the model for the demineralisation plant process module. A stream key is presented in Table 5.4 while the functions of the various building blocks associated with the normal cycle of operation and the various stages of the regeneration sequence are described in Table 5.5. Further comments regarding the modelling follow these tables.
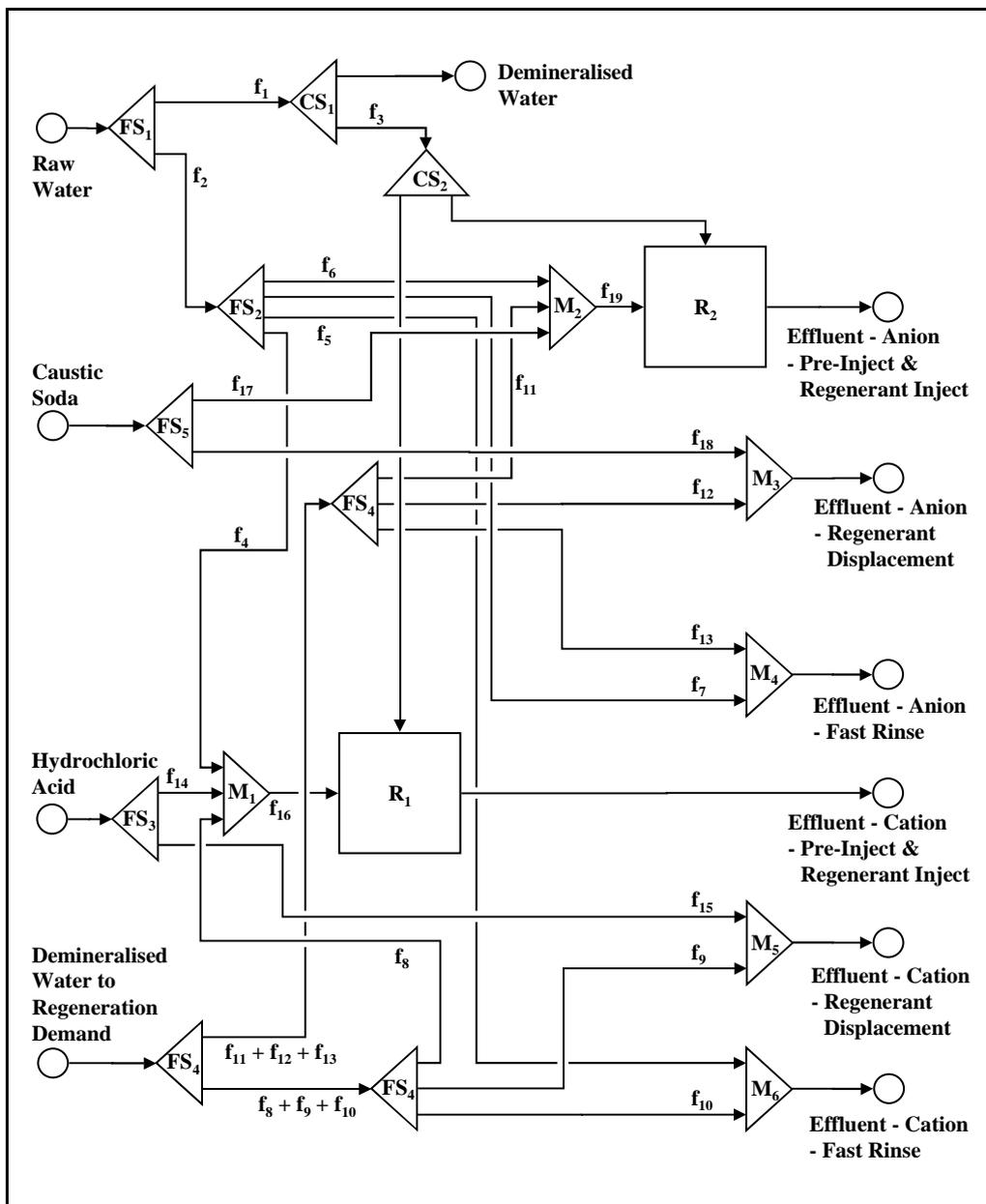
Figure 5.3. *Diagram of the model for the demineralisation plant process module.*

Table 5.4. *Stream key for the model for the demineralisation plant process module.*

Stream	Description
f_1	Mass flow of raw water to normal cycle of operation of demineralisation plant.
f_2	Mass flow of raw water to regeneration part of model.
f_3	Mass flow of ions (as salts) removed during demineralisation to regeneration part of model.
f_4	Mass flow of raw water to cation regeneration Pre-Inject & Regenerant Inject stage.
f_5	Mass flow of raw water to cation regeneration Fast Rinse stage.
f_6	Mass flow of raw water to anion regeneration Pre-Inject & Regenerant Inject stage.
f_7	Mass flow of raw water to anion regeneration Fast Rinse stage.
f_8	Mass flow of demineralised water to cation regeneration Pre-Inject & Regenerant Inject stage.
f_9	Mass flow of demineralised water to cation regeneration Regenerant Displacement stage.
f_{10}	Mass flow representing the demineralised water hold-up from cation regeneration Regenerant Displacement stage to cation regeneration Fast Rinse stage.
f_{11}	Mass flow of demineralised water to anion regeneration Pre-Inject & Regenerant Inject stage.
f_{12}	Mass flow of demineralised water to anion regeneration Regenerant Displacement stage.
f_{13}	Mass flow representing the demineralised water hold-up from anion regeneration Regenerant Displacement stage to anion regeneration Fast Rinse stage.
f_{14}	Mass flow of hydrochloric acid to cation regeneration Pre-Inject & Regenerant Inject stage.
f_{15}	Mass flow of hydrochloric acid hold-up from cation regeneration Pre-Inject & Regenerant Inject stage to cation regeneration Regenerant Displacement stage.
f_{16}	Mass flow of raw water, demineralised water and hydrochloric acid to cation regeneration Pre-Inject & Regenerant Inject stage reaction block.
f_{17}	Mass flow of caustic soda to anion regeneration Pre-Inject & Regenerant Inject stage.
f_{18}	Mass flow of caustic soda hold-up from anion regeneration Pre-Inject & Regenerant Inject stage to anion regeneration Regenerant Displacement stage.
f_{19}	Mass flow of raw water, demineralised water and caustic soda to anion regeneration Pre-Inject & Regenerant Inject stage reaction block.

Table 5.5. *The functions of the various building blocks associated with the model for the demineralisation plant process module.*

Building Block	Function
FS_1	Divides the flow of raw water between the normal cycle of operation (f_1) and the regeneration sequence (f_2) of the demineralisation plant.
FS_2	Divides the flow of raw water between the cation-exchange regeneration part of the model and the anion-exchange regeneration part of the model. Two streams are sent to the cation-exchange regeneration part of the model (f_4 and f_5) and two streams are sent to the anion-exchange regeneration part of the model (f_6 and f_7).
FS_3	Associated with the cation-exchange regeneration part of the model. Divides the flow of hydrochloric acid between the Pre-Inject & Regenerant Inject stage (f_{14}) and the Regenerant Displacement stage (f_{15}). The Pre-Inject stage and the Regenerant Inject stage are represented as a single stage in the model.
FS_4	Divides the flow of demineralised water amongst the various stages of the regeneration sequence. f_8, f_9 and f_{10} are sent to the cation-exchange regeneration part of the model while f_{11}, f_{12} and f_{13} are sent to the anion-exchange part of the model. These streams are associated with the Pre-Inject & Regenerant Inject stage (f_8 and f_{11}), the Regenerant Displacement stage (f_9 and f_{12}) and the Fast Rinse stage (f_{10} and f_{13}).
FS_5	Associated with the anion-exchange regeneration part of the model. Divides the flow of caustic soda between the Pre-Inject & Regenerant Inject stage (f_{17}) and the Regenerant Displacement stage (f_{18}).
CS_1	Effects the removal of species (f_3) from the raw water being treated by the demineralisation plant (f_1) such that demineralised water is produced.
CS_2	Divides the species removed by CS_1 into ions which are sent to the cation-exchange and anion-exchange parts of the model.
M_1	Associated with the cation-exchange regeneration part of the model. Represents the combination of the raw water (f_4), demineralised water (f_8) and hydrochloric acid (f_{14}) for the Pre-Inject & Regenerant Inject stage. Stream f_{16} is produced.
M_2	Associated with the anion-exchange regeneration part of the model. Represents the combination of the raw water (f_6), demineralised water (f_{11}) and caustic soda (f_{17}) for the Pre-Inject & Regenerant Inject stage. Stream f_{19} is produced.
M_3	Associated with the anion-exchange regeneration part of the model. Represents the combination of the caustic soda hold-up from the Pre-Inject & Regenerant Inject stage (f_{18}) and the demineralised water effluent from the Regenerant Displacement stage (f_{12}).
M_4	Associated with the anion-exchange regeneration part of the model. Represents the combination of demineralised water hold-up from the Regenerant Displacement stage (f_{13}) and the raw water effluent from the Fast Rinse stage (f_7).
M_5	Associated with the cation-exchange regeneration part of the model. Represents the combination of the hydrochloric acid hold-up from the Pre-Inject & Regenerant Inject stage (f_{15}) and the demineralised water effluent from the Regenerant Displacement stage (f_9).

cont.

Table 5.5. *cont.*

Building Block	Function
M_6	Associated with the cation-exchange regeneration part of the model. Represents the combination of demineralised water hold-up from the Regenerant Displacement stage (f_5) and the raw water effluent from the Fast Rinse stage (f_{10}).
R_1	Associated with the cation-exchange regeneration part of the model. Represents the removal of cations from the cation-exchange resin by the regenerant.
R_2	Associated with the anion-exchange regeneration part of the model. Represents the removal of anions from the anion-exchange resin by the regenerant.

The following points are raised with regard to the model for the demineralisation plant process module:

- As noted previously, at the changeover from the normal cycle of operation to the regeneration cycle of operation, the resin beds contain raw water. Clearly, this hold-up volume is of the same quality as the raw water being processed by the demineralisation plant. Making the assumption that the raw water used by the Fast Rinse stage is of the same quality as the raw water processed by the demineralisation plant, the demineralisation plant is modelled as having only a single raw water demand associated with it. Flow separator FS_1 is used to represent the flow split between the raw water used for the normal ion-exchange cycle of operation and the raw water involved in the regeneration cycle of operation.

  Raw water is involved in the regeneration procedure at three stages. These stages are as follows:

  - At the start of the regeneration procedure, the resin beds are filled with raw water

  - Raw water is used during the Fast Rinse stage

  - Raw water is present in the resin bed at the start of the Quality Rinse stage. This is the hold-up volume from the Fast Rinse stage. This water is recycled alongside the demineralised water used in the Quality Rinse stage as a process requirement and is thus eventually used in the production of demineralised water.

  From the above analysis, the raw water is only sent to the effluent in the first two instances. A flow-balance thus shows that the quantity of raw water that

becomes effluent is equivalent to the total volume used during the Fast Rinse stage. The modelling of the raw water distribution for the regeneration procedure therefore sees a mass of raw water, equivalent to the hold-up volume of the resin bed, being sent to the Pre-Inject stage; and a mass of raw water, equivalent to the portion of the Fast Rinse that is sent to effluent, being sent to the Fast Rinse stage. The Quality Rinse stage is not considered in the analysis since all water associated with this stage is recycled as a process requirement; any raw water associated with this stage becomes part of the demineralised water product. The distribution of raw water to the Pre-Inject and Fast Rinse stages of the regeneration sequence is represented by streams f_4-f_7 (Table 5.4).

- In terms of the raw water hold-up prior to the start of the regeneration procedure, it is noted that in reality a small portion of this water is displaced during the Pre-Inject stage with the remainder being displaced during the Regenerant Inject stage. However, with the volume of effluent associated with the Pre-Inject stage being very small, it is not economically viable to recover this effluent. The Pre-Inject and Regenerant Inject stages are therefore modelled together.

- Component separator CS_1 is used to represent the removal of ions from the raw water by the ion-exchange cycle of operation of the demineralisation plant. This process is modelled as the removal of salts from the raw water. These salts are divided into cations and anions by component separator CS_2 and sent to the cation-exchange regeneration and anion-exchange regeneration parts of the model. The Insolubles contaminant load is assumed to be divided equally between the cation-exchange bed and the anion-exchange bed.

- From the analysis presented on the flow of fluids through the demineralisation plant during the regeneration sequence in **Section 5.3.1.1**, it is noted that at the conclusion of any of the regeneration stages, with the exception of the Pre-Inject stage, the resin bed is filled with the fluid used during that particular regeneration stage. This hold-up volume is displaced by the fluid used in the succeeding stage and ends up in the effluent of the succeeding stage. This situation is represented by a combination of flow separators and mixers in the model for the demineralisation plant process module. Every regeneration stage has one flow separator and one mixer associated with it. The flow separator divides the flow to the regeneration stage into two portions. The first portion progresses to the mixer associated with that particular stage where it combines with the hold-up volume of fluid from the previous stage. The remaining portion of the flow from the flow separator, that is, the hold-up volume from the current stage, is sent to the mixer of the succeeding stage where it combines with the portion of the fluid passing through the resin bed during the succeeding stage.

- In the description of the basic building blocks presented in **Chapter 4**, it was noted that these elements were single functioned, that is, mixing blocks for stream combination or species addition; separation blocks for flow or component division; and, reaction blocks for chemical transformations. Seemingly, reaction blocks R_1 and R_2 represent a contradiction of this concept in that an addition function is combined with the chemical reaction function. In this situation however, it is ions that are being added and these are not defined as species in the model. As such they cannot be incorporated into the model using a mixer unit since such a unit only considers defined species. These ions undergo a chemical reaction with the regenerant species such that species defined in the model are produced. The reactions taking place during the regeneration of the cation-exchange bed are thus as follows:

$$Na^+ + HCl \rightarrow NaCl + H^+$$
5.1

$$Ca^{2+} + 2HCl \rightarrow CaCl_2 + 2H^+$$
5.2

$$Mg^{2+} + 2HCl \rightarrow MgCl_2 + 2H^+$$
5.3

and the reactions taking place during the regeneration of the anion-exchange bed are as follows:

$$Cl^- + NaOH \rightarrow NaCl + OH^-$$
5.4

$$SO_4^{2-} + 2NaOH \rightarrow Na_2SO_4 + 2OH^-$$
5.5

$$CO_3^{2-} + 2NaOH \rightarrow Na_2CO_3 + 2OH^-$$
5.6

Clearly HCl is modelled as a desirable species at the hydrochloric acid inlet to the process module while NaOH is modelled as a desirable species at the caustic soda inlet to the process module.

5.3.1.3 *Regeneration Frequency Considerations for the Demineralisation Plant*

Until this point in the discussion on the modelling of the demineralisation plant process module, there has been little consideration given to the regeneration frequency of the plant. The regeneration frequency is dependent on the quantity and quality of the water treated by the plant. A change in either of these factors will produce a change in the regeneration frequency. This will have implications for the quantities of regenerant chemicals required and the amount of effluent generated by the demineralisation plant subsystem. While the quantities of these materials and the effluent generated will be the same per regeneration cycle, the time-average quantities will be different. In addition, a change in the regeneration frequency will have implications on the rate of production of demineralised water.

The production rate of demineralised water achievable by the plant is 16 to 18 m³/h. This production rate is greater than the rate of demand within the complex. The excess production is stored in a tank such that a reserve is built up. During the regeneration sequence, no demineralised water is produced. Demands for demineralised water during this period are thus met using demineralised water from the reserve. A change in the regeneration frequency will affect the amount of demineralised water available in the reserve. At the current production rate, an increase in the regeneration frequency may result in a situation where there is insufficient water available in the reserve to satisfy demands in the complex during the regeneration period. To compensate for this possibility, the production of demineralised water must increase, but this can only occur up to the maximum production capacity of the plant.

The dependence of the demineralised water production rate on the regeneration frequency introduces a complication to the system under consideration. This complication can be overcome by formulating the problem in such a way that the production of a fixed quantity of demineralised water is considered rather than the rate at which this water is produced. Then, the only criteria that must be checked is that the required rate of production of demineralised water does not exceed the maximum rate achievable by the demineralisation plant.

In light of the preceding discussion, the model considers the production of an amount of demineralised water over one total cycle of operation at the current regeneration frequency, that is, the amount of water produced between two successive regenerations over a period of 16 h. A demineralised water production rate of 16 m³/h is assumed over the normal cycle of operation. The regeneration procedure lasts 191 min which means that the average rate of production over the total cycle of operation is 13.3 m³/h.

As noted above, the fixed amount of demineralised water considered in the model corresponds to the demineralised water production from one normal cycle of operation in the current operating configuration. In this configuration, the raw water used for the production of demineralised water is an equal ratio blend of Umgeni Water and Umbogintwini River water. Using this information, it is possible to determine the exchange capacity of the demineralisation plant for the removal of ions from the raw water. In terms of the regeneration of the plant, particular quantities of regenerants, demineralised water and raw water are required when the exchange capacity of the plant has been reached. The quantities of materials which correspond to the exchange capacity of the plant are considered to be reference points against which the regeneration requirements of other operating configurations are scaled. In particular, while the model considers the production of a fixed quantity of demineralised water, the quality associated with the influent water may change during the course of the optimisation; different quantities of regenerants, demineralised water and raw water will be required for regeneration by this new operating configuration. These quantities are proportional to the ionic load to be removed from the influent water. Thus, taking caustic soda as an example, the caustic soda regeneration requirement by any operating configuration is determined by:

$$f_{CS} = f_{CS,ec} \cdot \frac{LD}{LD_{ec}}$$

5.7

In this equation, f_{CS} represents the caustic soda requirement associated with a particular operating configuration and LD represents the total ionic load removed from the influent water for that configuration. LD_{ec} is the exchange capacity of the demineralisation plant and $F_{CS,ec}$ is the quantity of caustic soda required for regeneration when the ionic load removed from the influent water is equivalent to the exchange capacity of the demineralisation plant. Regarding the representation of the exchange capacity in terms of the total ionic load, it should be noted that the assumption is made that all species present in the influent water have the same probability of binding to an ion-exchange site on the ion-exchange resin.

5.3.1.4 *The Problem Statement for the Demineralisation Plant Subsystem*

Figure 5.4 shows the demineralisation plant process module integrated with the external sources and terminal sinks present in the superstructure as a representation of the overall optimisation problem for the demineralisation plant subsystem. The GAMS coding for this model is presented on the **CD** which accompanies this thesis. The objective function of this problem may be stated as follows:

> *The system comprises the demineralisation plant process module. Given two different sources of raw water, together with sources of hydrochloric acid and caustic soda, the task is to identify an optimal network configuration which achieves the required rate of production of demineralised water at the lowest cost. This cost includes the costs associated with the replacement of the cation-exchange and anion-exchange resins, the purchase of external sources and the disposal of the effluents produced by the system.*

The following points are made with regard to the objective function for the problem:

- The objective function does not include capital costs. Given that this is a retrofit problem, capital costs extend mainly to the installation of new piping rather than the purchase of costly equipment. Additional storage capacity may also be required. It is however assumed that the savings in operating costs through the more efficient use of water and materials are sufficient to offset the costs associated with effecting these minor changes to the process system. Capital costs are thus not considered explicitly.

- A cost factor associated with the replacement of the ion-exchange resins is included in the objective function for the problem. In practice, a portion of the ion-exchange resin needs to be replaced annually due to resin losses and resin fracture. This portion is related to the number of regeneration cycles taking place annually and is thus also related to the total ionic load removed from the influent water. The incorporation of the regeneration resin replacement costs into the Pinch Analysis involves the incorporation of an additional term in the

objective function described by Equation 4.12. For this problem, the objective
function therefore takes the form:

$$TC = \sum_h CST^{PSRC}_h \cdot F^{PSRC}_h + \sum_i CST^{SSRC}_i \cdot F^{SSRC}_i$$

$$+ \sum_j CST^{SNK}_j \cdot F^{SNK}_j + CST_{RESIN} \cdot \frac{LD}{LD_{ec}} \qquad 5.8$$

where TC is the total operating cost, CST^{PSRC}_h is the cost factor associated with the use of
primary source h, CST^{SSRC}_i is the cost factor associated with the use of secondary source i,
CST^{SNK}_j is the cost factor associated with sink j and CST_{RESIN} is the current resin replacement
cost per regeneration. F^{PSRC}_h is the total mass flow from primary source h, F^{SSRC}_i is the total
mass flow from secondary source i, F^{SNK}_j is the total mass flow to sink j. As previously, LD
represents the total ionic load removed from the influent water and LD_{ec} is the exchange
capacity of the demineralisation plant.
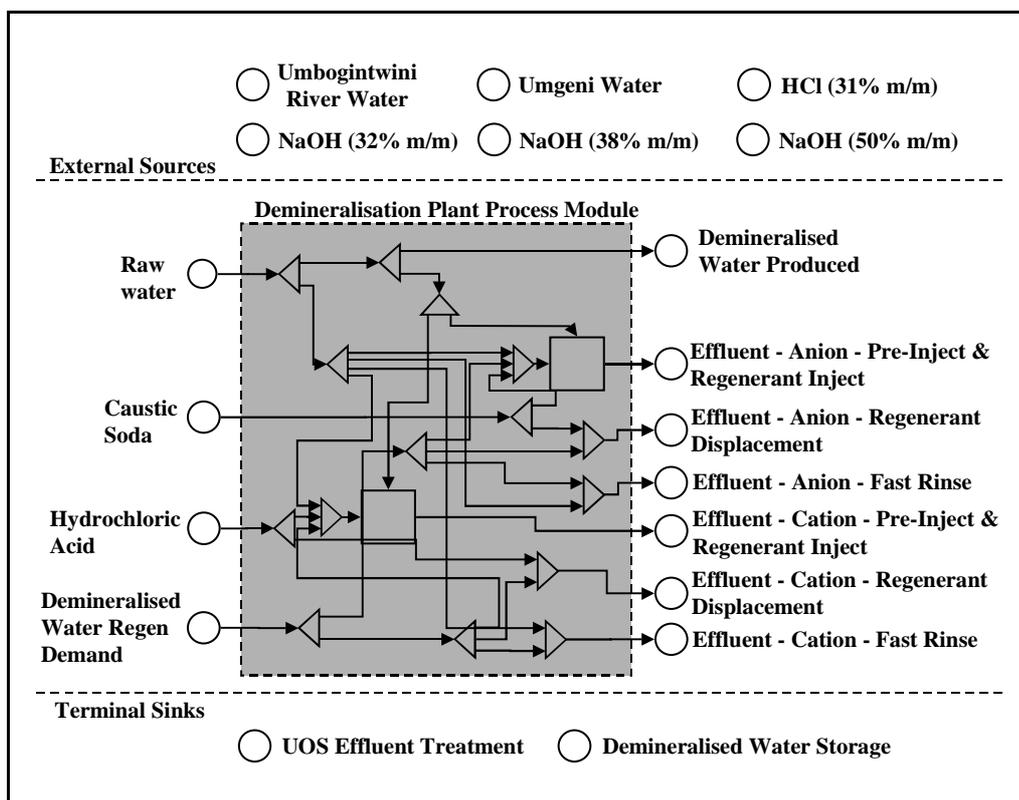
Figure 5.4. *Diagram showing the integration of the demineralisation plant process
module with the external sources and terminal sinks present in the
superstructure as a representation of the overall optimisation problem
for the demineralisation plant subsystem.*

Table 5.6 presents the results obtained from the optimisation problem which was solved using
GAMS CONOPT. These results are analysed in **Chapter 6** and further consideration is
deferred until then. The proposed network configuration is presented in Figure 5.5.

Table 5.6. *Comparison of water and material requirements and effluent production associated with the existing network configuration and the optimal network configuration. A fixed amount of demineralised water is produced by both configurations.*

	Unit	Existing Configuration	Optimal Configuration
Demineralised Water Produced	[t]	254.87	254.87
Number of Regeneration Cycles	[ ]	1	1.22
Umbogintwini River Water	[t]	130.45	254.93
Umgeni Water	[t]	130.45	0
Total Water	[t]	260.90	254.93
Hydrochloric Acid (31% m/m HCl)	[kg]	350.00	366.42
Caustic Soda (32% m/m NaOH)	[kg]	390.00	407.70
Caustic Soda (38% m/m NaOH)	[kg]	0	0
Caustic Soda (50% m/m NaOH)	[kg]	0	0
Demineralised Water Available to Other Subsystems	[t]	239.20	241.18
Effluent	[t]	22.42	14.51
NaCl Load to Effluent	[kg]	195.13	202.64

Figure 5.5. *Diagram showing the optimal network configuration for the demineralisation plant subsystem.*

5.3.2 The Chemical Production Subsystem

The chemical production subsystem includes the brine circuit, the hydrogen and chlorine processing plants, the caustic evaporators, the hydrochloric acid synthesis plant, the sodium hypochlorite synthesis plant, the Hydecat destruction plant, and a number of other associated demands and sources of water located within the chlor-alkali complex. This subsection considers the optimisation of the chemical production subsystem in isolation from the other subsystems. Allowance is however made for the various interdependencies that exist between the chemical production subsystem and the demineralisation plant subsystem such that these may still be met by the optimised system. In addressing these interdependencies, the following points are noted:

- The cost associated with the use of demineralised water is taken to be the unit cost of demineralised water associated with the existing production strategy, that is, the current raw water quality, rate of production of demineralised water and regeneration frequency.

- The amounts of caustic soda and hydrochloric acid required for the regeneration of the demineralisation plant are similarly taken to be the amounts associated with the existing production strategy, that is, the current raw water quality, rate of production of demineralised water and regeneration frequency.

In addition, the production levels of chlorine gas, sodium hypochlorite and hydrochloric acid are maintained at their current levels. The rates of production of caustic soda and hydrogen gas are dependent on the chlorine production rate and are thus automatically maintained at the existing levels. Similarly, the amount of off-specification or excess sodium hypochlorite produced by the complex and handled by the Hydecat destruction plant is considered constant.

Figure 5.6 shows the chemical production subsystem in terms of its constituent plants. Each of these divisions in turn may consist of a number of process modules. Having already demonstrated, via the example of the demineralisation plant process module, the types of assumptions required in modelling the process modules and how process modules are assembled from the four basic building blocks presented in **Chapter 4**, consideration of these issues for the process modules associated with the chemical production subsystem will not be presented here. Instead only an overview of the various process modules will be provided, with the assumptions and detailed modelling considerations being presented in **Appendix C**. The mathematical description of these process modules is presented within the GAMS coding which is included on the **CD** accompanying this thesis. The order of presentation of the plants which constitute the chemical production subsystem is thus as follows: **Section 5.3.2.1** presents the description of the process modules associated with the brine circuit; **Section 5.3.2.2** presents the process modules associated with the product processing and support operations, that is, the caustic evaporation plant process module, the hydrochloric acid synthesis process module, the sodium hypochlorite synthesis process module, the Hydecat destruction process

module and the various point sources and demands located on the complex. **Section 5.3.2.3** presents some final comments on the modelling and optimisation of the chemical production subsystem and presents the problem statement for the chemical production subsystem.
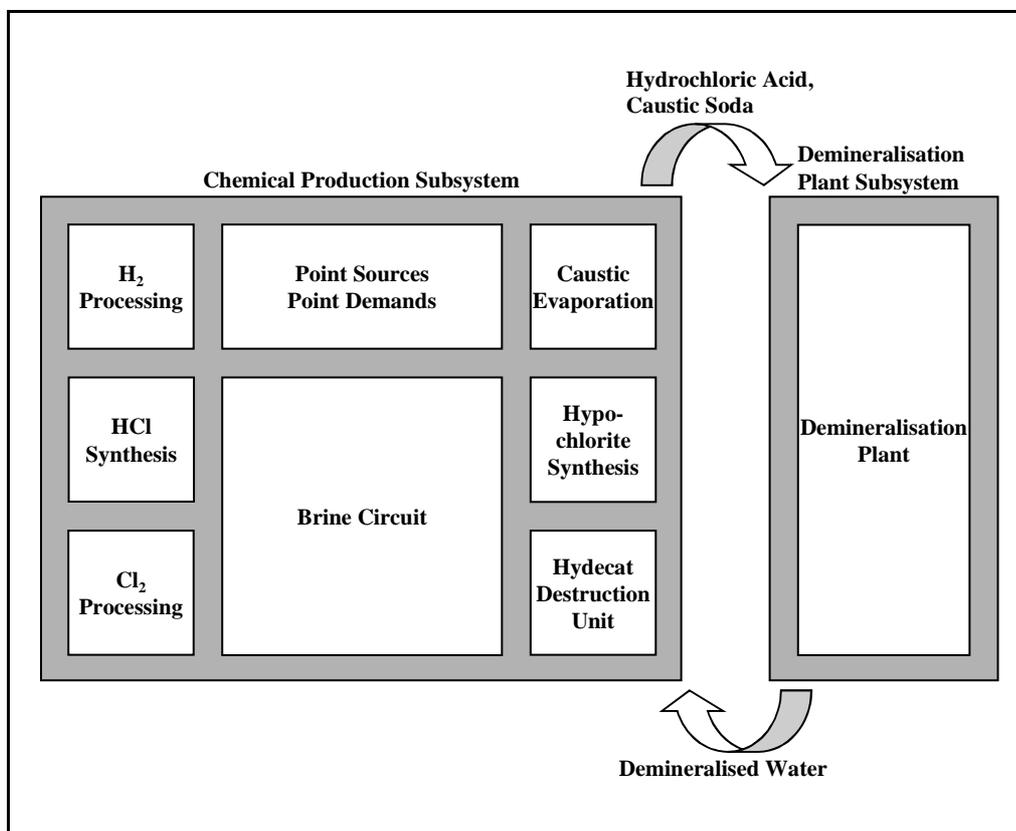
Figure 5.6. *Diagram showing the constituent plants of the chemical production subsystem and the existing interactions between the chemical production subsystem and the demineralisation plant subsystem.*

5.3.2.1 *The Brine Circuit*

The brine circuit constitutes the major component of the chemical production subsystem and the various operations making up the circuit are modelled as a number of process modules. Before these process modules are considered however, a number of general concepts pertaining to the modelling of the subsystem are presented.

Figure 5.7 presents the simplified process flow diagram of the brine circuit previously presented as Figure 3.2. As was noted in **Chapter 3**, a series of raw material purification steps precede the electrolyser and condition the brine to a standard acceptable to the electrolyser. The chief contaminants that these operations remove are calcium and magnesium which are introduced alongside the sodium chloride in the raw salt added to the system at the resaturator. As has also been noted previously trace quantities of other contaminants enter the brine circuit

alongside the calcium and magnesium in the raw salt. As such, the following is assumed regarding the sequence of the purification steps:

- From the perspective of removing calcium and magnesium from the brine circuit, the sequence of operations is assumed to be economically optimal and all operations in the sequence are required.

- From the perspective of the other trace contaminants present in the brine, the different operations are assumed collectively to reduce the concentrations of these species to levels acceptable to the operation of the plant.
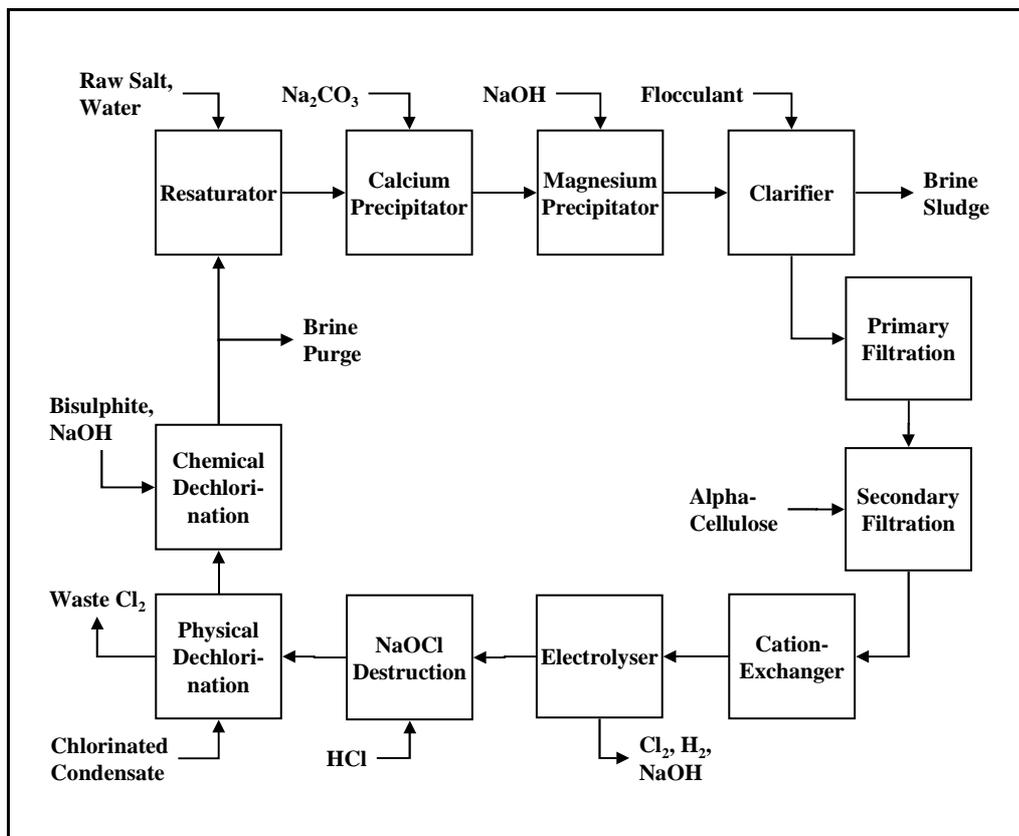
Figure 5.7. *Schematic diagram of the brine circuit at the Sasol Polymers chlor-alkali complex at Umbogintwini. Secondary streams associated with the cation-exchange regeneration procedure and the backwash of the primary filter are not shown.*

In light of these assumptions, the sequence of the raw material purification operations preceding the electrolyser is considered fixed. Reuse opportunities for water and materials are built around this structure. In addition, with the raw salt representing the only source of the trace contaminants, the effects of these contaminants are considered negligible provided that they pass through the entire sequence of purification steps. These species are thus not considered explicitly in the Pinch Analysis.

While it is possible to ignore the trace species, since they are only present in the raw salt, calcium and magnesium are present in other sources used within the circuit. In particular, calcium and magnesium may be present in other sources available within the complex and which could be reused in the brine circuit. Hence it is necessary to determine whether the cost associated with removing the additional loads of calcium and magnesium in the circuit is offset by the benefits accrued from the recovery of these sources.

Figure 5.8 presents the brine circuit as a collection of process modules. These process modules include the electrolyser, primary dechlorination, secondary dechlorination, precipitation, clarification, primary filtration, secondary filtration and cation-exchange. It should be noted that while the brine circuit is modelled as a collection of process modules, the required sequence of the raw material purification steps is established by the incorporation of the necessary logic into the connectivity matrix.

The Brine Circuit

Secondary Dechlorination	Precipitation	Clarification
Primary Dechlorination		Primary Filtration
Electrolyser	Ion-Exchange	Secondary Filtration
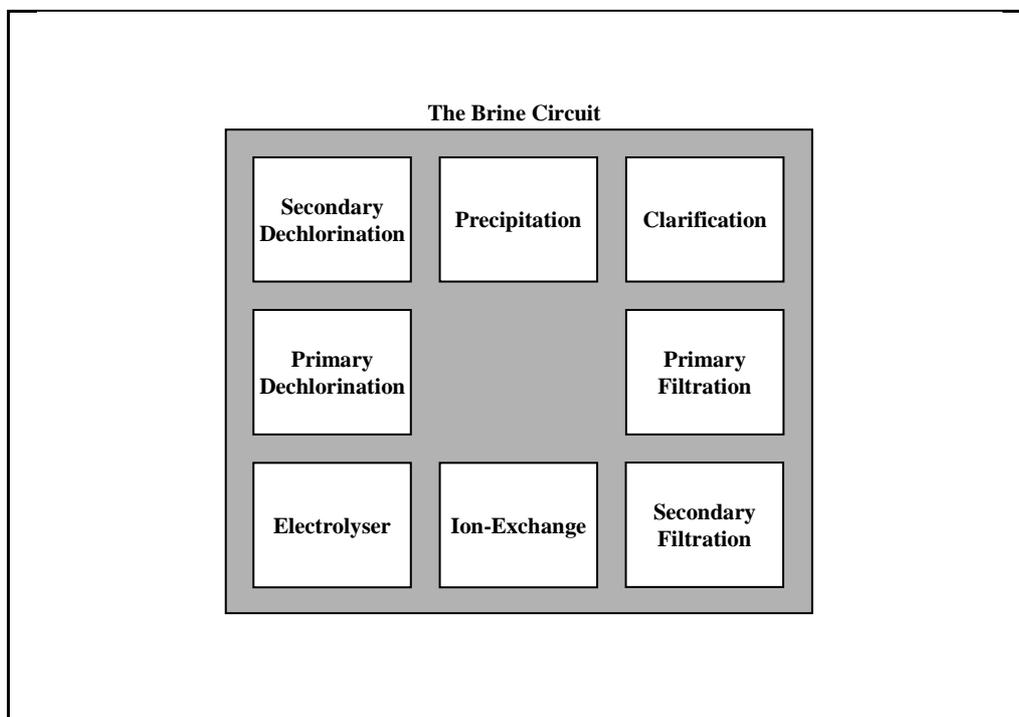
Figure 5.8. *Diagram showing the brine circuit as a collection of process modules considered in the optimisation of the chemical production subsystem.*

In comparing Figure 5.8 with Figure 5.7, it will be noticed that certain aspects of the brine circuit are not present as process modules, notably the resaturator, the NaOCl destruction step and the brine purge. The resaturator is included indirectly via constraints at the electrolyser and the precipitation process modules and through the logic of the connectivity matrix. The NaOCl destruction step is combined with the electrolyser. In terms of the representation of the brine purge, it should be noted that all flow splits currently in the brine circuit are not represented because these will be reconfigured during the optimisation. In particular, the

function of the brine purge in the circuit is to maintain the concentrations of certain species below their maximum limits. Therefore its flowrate and position will be established according to the various species concentration limits.

The process modules making up the brine circuit are now considered in greater detail.

The Electrolyser Process Module

While the operations preceding the electrolyser all handle the concentrated brine solution, none of these operations has any specific requirement for the species NaCl. The electrolyser however requires a specific flowrate of brine and a specific concentration of sodium chloride such that the required production levels of chlorine gas and correspondingly caustic soda and hydrogen gas may be achieved. NaCl is thus modelled as a desirable species at the inlet to the electrolyser and it is this constraint that establishes the rate of addition of the raw salt to the circuit.

With there being a tight specification on the concentration of the species in the brine entering the electrolyser, and, in particular, with the concentration of sodium chloride being held constant and the flow of brine being fixed, the molar extents of the reactions taking place in the electrolyser are assumed to be the same as those associated with the current operating conditions. In terms of the species of interest for the Pinch Analysis, these reactions take the form:

$$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O \qquad\qquad 5.9$$

$$3NaOCl \rightarrow NaClO_3 + 2NaCl \qquad\qquad 5.10$$

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2 \qquad\qquad 5.11$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad\qquad 5.12$$
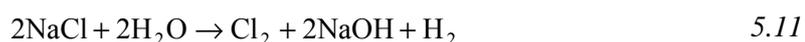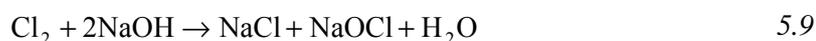
The electrolyser process module comprises elements which model the conversion of NaCl to products and by-products, the transfer of species across the membrane into the caustic soda solution and the processing of the chlorine and hydrogen gases produced by the electrolyser. In addition, the process module includes an element for the dosing of hydrochloric acid to the lean brine emerging from the electrolyser. In terms of this dosing, the assumption is made that the molar ratio of hydrochloric acid to sodium hypochlorite in the lean brine must be the same as the ratio currently supplied. Representing the dosing operation in this way encourages the recovery of HCl-containing sources present on the complex. Clearly, HCl is modelled as a desirable species in this situation.

Overall, there are three demands and five sources associated with the electrolyser process module. The demands are for brine, demineralised water (a process requirement) and hydrochloric acid while the sources produced by the process module are treated brine, caustic soda and condensate from the chlorine and hydrogen coolers and hydrogen chiller. The treated

brine is routed to the primary dechlorination process module as a process requirement. The caustic soda may be used within the complex or is routed to the caustic evaporators. The condensate from the chlorine cooler may be sent to either of the dechlorination stages or to the sodium hypochlorite synthesis process module. No restrictions are placed on the routing of the condensate from the hydrogen cooler and chiller.

The Primary Dechlorination Process Module

The primary dechlorinator uses air to strip chlorine from the brine stream. Alongside the removal of chlorine, water is also removed from the brine. The quantity of water removed from the brine is assumed to be the same as that currently removed by the dechlorinators while the removal of chlorine is represented by a removal ratio. The primary dechlorination process module has a single brine inlet and produces two sources of material, that is, a dechlorinated brine stream and a waste chlorine stream. The dechlorinated brine is sent to the secondary dechlorination stage as a process requirement while the waste chlorine stream is sent to the sodium hypochlorite synthesis process module.

The Secondary Dechlorination Process Module

The secondary dechlorination process module has three demands associated with it, that is, brine, caustic soda and sodium bisulphite. Caustic soda is used for the neutralisation of any hydrochloric acid remaining in the brine coming from the primary dechlorination stage while sodium bisulphite is added to destroy residual chlorine present in the brine. These reactions take place according to:

$$HCl + NaOH \rightarrow NaCl + H_2O \qquad\qquad 5.13$$

$$Cl_2 + 3NaOH + NaHSO_3 \rightarrow Na_2SO_4 + 2NaCl + 2H_2O \qquad\qquad 5.14$$
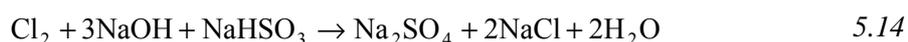
The molar extents of these reactions are based on residual concentrations of $NaHSO_3$ and Cl_2 in the brine source emerging from the process module[1]. Complete neutralisation of HCl is assumed. NaOH is modelled as a desirable species at the caustic soda inlet to the process module while $NaHSO_3$ is modelled as a desirable species at the sodium bisulphite inlet to the process module. Brine from the secondary dechlorination process module is routed to the precipitation process module or to the effluent terminal sink.

As a general comment, it should be noted that the possibility of a connection between each brine source emerging from the various process modules, with the exception of the electrolyser and the primary dechlorination process modules, and the final effluent terminal sink is included in the connectivity matrix. With the loads of several species in the brine circuit being controlled by the purge, these possibilities will allow the optimisation to determine the optimal

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[1] *In terms of the modelling, the assumption is made that all $NaHSO_3$ is converted to Na_2SO_4. The $NaHSO_3$ concentration at the outlet of the secondary dechlorination process module is thus considered to be zero. A more detailed discussion of this issue is however presented in **Appendix C**.*

location of the purge stream. The potential routing of streams to the effluent terminal sink is taken as being implicit in all process modules considered henceforth.

The Precipitation Process Module

Both the precipitation of calcium as calcium carbonate (Equation 5.16) and the precipitation of magnesium as magnesium hydroxide (Equation 5.17) are represented in the precipitation process module. Given the nature of the relationships governing the precipitation process, it is considered appropriate to consider some of the assumptions involved in the modelling of this process module in greater detail.

$$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3 \qquad\qquad 5.16$$

$$MgCl_2 + 2NaOH \rightarrow 2NaCl + Mg(OH)_2 \qquad\qquad 5.17$$
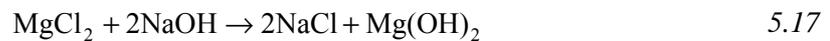
The amount of calcium carbonate and magnesium hydroxide that precipitates from the brine solution is controlled by an equilibrium solubility product. The solubility product is the name given to the equilibrium constant for the reaction in which a precipitate dissolves in pure water to yield its constituent ions (Snoeyink and Jenkins, 1980). For the precipitation of calcium carbonate the solubility product takes the form:

$$[Ca^{2+}] \cdot [CO_3^{2-}] = K_{sp,CaCO_3} \qquad\qquad 5.18$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the molar concentrations of calcium cations and carbonate anions in solution and $K_{sp,CaCO3}$ is the equilibrium solubility product constant for calcium carbonate[1]. Similarly, the solubility product for the precipitation of magnesium hydroxide takes the form:

$$[Mg^{2+}] \cdot [OH^-]^2 = K_{sp,Mg(OH)_2} \qquad\qquad 5.19$$

where $[Mg^{2+}]$ and $[OH^-]$ are the molar concentrations of the magnesium cations and the hydroxide anions and $K_{sp,Mg(OH)2}$ is the equilibrium solubility product constant for magnesium hydroxide.

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[1] *Strictly speaking, the solubility product involves the activities of the ions rather than the true concentrations. Equations 5.18-5.19 are valid only when the activity coefficients for the ions are unity as is the case for extremely dilute solutions. The activity coefficient is the ratio between the apparent or active concentration of a substance and the true concentration of the substance. It is possible to lump the activity coefficients into K_{sp}, to yield the 'apparent' solubility product. This is chiefly influenced by the ionic strength, which, in this example, is likely to remain relatively constant. The 'apparent' solubility product is thus largely a function of the true concentration only, A more detailed treatment of this topic is presented by Snoeyink and Jenkins (1980).*

As a means of illustrating the next point, the precipitation of calcium carbonate is considered in the following discussion. At equilibrium, the concentration of calcium cations in solution is related to the concentration of carbonate anions in solution via the solubility product.   If additional sodium carbonate is added to the solution, the equilibrium will shift such that more calcium carbonate precipitates.   This results in a lowering of the concentration of calcium cations in solution. Figure 5.9 illustrates the relationship between the concentration of calcium cations and carbonate anions in solution.
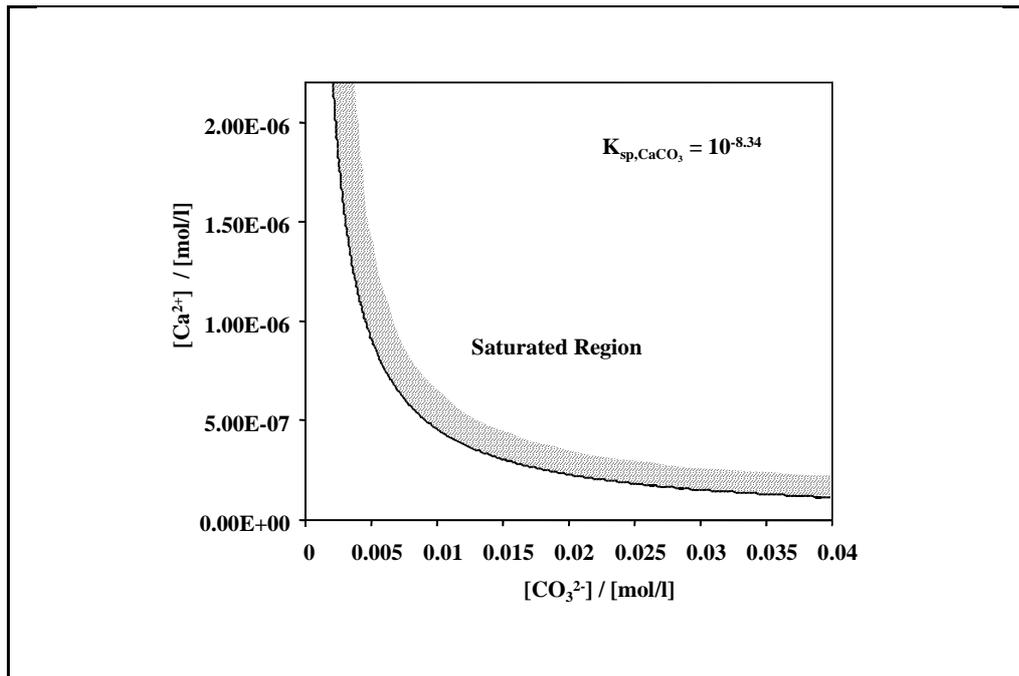
Figure 5.9. *Plot of the calcium cation molar concentration $[Ca^{2+}]$ in solution versus the carbonate anion molar concentration $[CO_3^{2-}]$ in solution at equilibrium. These concentrations are related by the solubility product $K_{sp,CaCO3}$, the value of which is taken from Snoeyink and Jenkins (1980).*

At higher concentrations of calcium cations, the quantity of sodium carbonate required to precipitate a unit of calcium carbonate is lower than that required at lower concentrations of calcium cations. Within the brine circuit, precipitation forms part of the series of operational steps employed to reduce the concentration of calcium cations in the brine solution. For each of these steps, there is a cost associated with the removal of a single unit of calcium cations from solution. Ideally this cost should increase in the direction of decreasing calcium cation concentration, which is the assumption already made for the brine circuit. Precipitation is typically an operation which is cost effective in removing species from solution when the concentration of that species is relatively high.   As the cost associated with precipitation increases with decreasing species concentration, a point is reached where another unit operation within the series of purification steps becomes more cost effective in achieving further reductions in the species concentration. This point corresponds to a unique set of

solution ion concentrations.   The assumption is thus made that the existing set of concentrations for calcium and magnesium cations, and carbonate and hydroxide anions in solution at the outlet of the precipitation operation corresponds to this point. The result of this assumption is that the precipitation process may be modelled in terms of fixed outlet concentrations rather than the solubility product type constraints represented by Equations 5.18 and 5.19. This is advantageous for the model since constraints of the form represented by Equations 5.18 and 5.19 are difficult to handle in the optimisation. The required dose of sodium carbonate and caustic soda is then determined by the optimisation.

The precipitation process module has associated with it three demands and one source. The demands correspond to demands for brine, caustic soda and sodium carbonate. Clearly Na_2CO_3 is modelled as a desirable species at the sodium carbonate inlet of the precipitation process module while NaOH is modelled as a desirable species at the caustic soda inlet of the precipitation process module. As previously noted the brine inlet is the only point at which raw salt is permitted to enter the brine circuit. The brine stream emerging from the process module is routed to the clarification process module.

The Clarification Process Module

The function of this process module is the removal of insoluble matter from the brine stream as brine sludge. Two demands and two sources are associated with the process module. The demands are for brine and flocculant while the sources produced by the process module are a brine sludge stream and a clarified brine stream. The dosing of flocculant is assumed to be proportional to the amount of solid material removed from the brine stream. The flocculant itself is not represented in the model since the assumption is made that it is completely removed by the clarification process; only the dilution water accompanying the flocculant addition to the brine is represented in the model. A suitable cost factor is attached to the dilution water demand to account for the cost of water and flocculant. The removal of solids is modelled in terms of a removal ratio and the total solids fraction associated with the brine sludge is assumed constant. The brine sludge stream emerging from the process module is routed to the terminal effluent sink while the clarified brine is routed to the primary filtration process module.

The Primary Filtration Process Module

Both the normal cycle of operation and the backwash cycle, on a time-average basis, are represented in the model for the primary filtration process module. Correspondingly, there are two demands and two sources associated with this process module. The demands are for brine by the normal cycle of operation and by the backwash cycle of operation. The demand by the backwash cycle is assumed proportional to the amount of material removed by the filter. A removal ratio is used to represent the removal of insoluble matter from the brine stream while removal ratios are also used to represent the concentration differences of calcium and magnesium observed across the filter. These solids are transferred from the normal cycle of operation of the filter to the backwash cycle. The brine stream emerging from the normal cycle of operation is currently only routed to the secondary filtration process module, but may be

routed to the backwash cycle of the primary filtration process module if deemed appropriate by the optimisation. Brine from the backwash cycle is routed to the clarification process module.

The Secondary Filtration Process Module

The secondary filtration process module has two demands and two sources associated with it. These demands are for brine and for alpha-cellulose. The secondary filtration stage uses candle filters, and alpha-cellulose is used as the filter aid. The amount of alpha-cellulose dosed to the brine is assumed proportional to the material removed by the filter. The alpha-cellulose itself is not represented in the model since it is completely removed during the filtration stage and only the water accompanying its addition is represented. A suitable cost factor is however attached to the alpha-cellulose inlet to account for the purchase cost associated with the alpha-cellulose. The removal of material is modelled using a removal ratio for insoluble material; removal ratios are also used to represent the calcium and magnesium concentration differences observed across the filter. The brine stream emerging from the process module is routed to the cation-exchange process module and possibly to the backwash cycle of the primary filtration process module. Although not strictly correct in terms of what occurs on the plant, the solids removed by the filtration process (excluding the spent filter medium) are routed to the terminal effluent treatment sink. An appropriate cost factor is however applied to the material removed by the filter to represent the cost associated with the disposal of this solid waste.

The Cation-Exchange Process Module

The cation-exchange process module is similar to the demineralisation plant process module and both the normal cycle of operation and the regeneration cycle of operation are considered. The process module has two demands for brine, one by the normal cycle of operation and one by the regeneration cycle of operation, and demands for hydrochloric acid, caustic soda and water. Eight sources are associated with the process module. Apart from the brine stream emerging from the normal cycle of operation which is routed to the electrolyser process module, there are seven sources associated with the regeneration cycle of operation emerging from the process module. These sources correspond to the seven stages of the regeneration procedure, that is, Brine Displacement, Backwash, Acid Regeneration, Acid Displacement, Caustic Regeneration, Caustic Displacement and Brine Replacement. The possible reuse opportunities for these effluents are as follows:

- The effluents from the Brine Displacement and Brine Replacement stages are mixtures of demineralised water and polished brine. These effluents could be recycled to the brine circuit.

- Effluent from the Backwash stage is assumed to be of demineralised water quality but may have some filterable material present in it. This effluent could be recycled to the brine circuit, possibly at some point before the filtration stage.

- The effluents from the Caustic Regeneration and Caustic Rinse stages are both mixtures of demineralised water and caustic soda. These effluents could be reused directly in the preparation of the caustic soda requirement for the succeeding regeneration cycle or elsewhere in the chemical production subsystem.

- Effluent from the Acid Rinse stage is a mixture of hydrochloric acid and demineralised water. This effluent could be reused when the hydrochloric acid requirement for the succeeding regeneration cycle is prepared.

- Effluent from the Acid Regeneration stage is a mixture of hydrochloric acid, demineralised water and cations eluted from the cation-exchange resin. This effluent is thus a mixture of desirable species (HCl) and undesirable species ($CaCl_2$ and $MgCl_2$).

  In practice, ion-exchange is typically a final polishing step in a series of purification steps. Much of the cation load entering the brine circuit will thus have been removed by this stage and the cation load associated with the effluent is therefore not large. Clearly, with some hydrochloric acid being present in the effluent, there is a certain inherent value associated with this effluent. Conceivably, the effluent could be used in the hydrochloric acid dosing of the brine in the electrolyser process module. The question is however raised as to whether the cost associated with the removal of an additional load of cations from the circuit is offset by the savings accrued from the recovery of HCl.

The above possibilities are included in the connectivity matrix of the chemical production subsystem. With these reuse possibilities, the assumption is again made that the effluents are well mixed.

5.3.2.2 *Product Processing and Support Operations*

These operations make up the remainder of the chemical production subsystem. Amongst the product processing operations are the caustic evaporators, the hydrochloric acid synthesis plant and the sodium hypochlorite synthesis plant. The support operations include the Hydecat destruction plant, the pump seals and the various other point sources and demands present within the chlor-alkali complex.

The Caustic Evaporation Plant Process Module

This process module has two demands and four sources associated with it. The demands correspond to the inlets for caustic soda to the first and second effects while two of the sources correspond to the concentrated caustic soda produced by the first and second effects. The remaining sources correspond to the steam condensate produced by the first effect and the

process condensate removed from the caustic soda during the evaporation process. The steam required by the first effect is assumed to be proportional to the caustic soda throughput.

Two terminal storage sinks are included in the superstructure to accept any concentrated caustic soda from either the first or second effect of the caustic evaporator. Both of these sinks have an appropriate cost factor associated with them which provides an incentive for caustic soda to be sent to these sinks as opposed to the effluent sink.

The Hydrochloric Acid Synthesis Process Module

Given that the quality of the hydrochloric acid product produced by the complex must be within a narrow specification for reasons of marketability, a tight specification exists at the inlet to the hydrochloric acid synthesis plant. The raw materials used in the production of hydrochloric acid are hydrogen gas, chlorine gas and demineralised water. With there being no alternative network configurations for the routing of materials to the hydrochloric acid synthesis plant, that is, there are no other acceptable sources of raw materials present in the complex except those currently used, the hydrochloric acid synthesis plant is not considered in the optimisation. The hydrochloric acid product is however available for use in the rest of the complex.

The hydrogen chloride scrubber associated with the elimination of gaseous hydrogen chloride released from the hydrochloric acid product storage vessels is however represented in the process module. This scrubber has a single caustic soda demand and produces a single caustic soda source. With the amount of hydrochloric acid produced by the complex being constant, the mass-load of gaseous hydrogen chloride entering the scrubber is considered fixed. The caustic soda effluent is available for reuse at a demand requiring caustic soda. NaOH is modelled as a desirable species at the inlet of the scrubber.

The Sodium Hypochlorite Plant Process Module

Unlike the case of the hydrochloric acid synthesis plant, raw materials for the production of sodium hypochlorite may be drawn from a number of sources within the complex. The sodium hypochlorite plant is thus included in the optimisation model and is represented by a demand requiring a specific flowrate of material. Here, Cl_2 and NaOH are modelled as desirable species. The amount of waste sodium hypochlorite sent to the Hydecat destruction process module is considered fixed.

The Hydecat Destruction Process Module

The function of this process module is the destruction of the excess or off-specification sodium hypochlorite. The process module has a single demand associated with it and produces a single source. Waste sodium hypochlorite and steam are sent to this demand as enforced matches; dilution water is added to this mixture such that the concentration of NaOCl is below the maximum permitted by the operation. Umbogintwini River water is used for this purpose in the existing network configuration. The effluent produced by the process module has a

relatively high concentration of NaCl and the recovery of this effluent may be a possibility. Alternatively, this effluent is routed to the effluent terminal sink.

Point Sources and Demands

A number of point sources and demands are present on the complex. The point sources include effluent from the chlorine filter, pump seals and condensate from a number of different sources such as the brine and catholyte heat-exchangers, intercondensors and other steam traps. With the exception of the effluent from the chlorine filter, which has a concentration of chlorine associated with it, these sources are assumed to have a quality close to that of demineralised water[1]. While other point sources do exist, such as the effluents from plant washing, pressure testing and cylinder steaming, these effluents are considered by the plant engineers to be either too contaminated for reuse or too difficult to recover and are not considered in the Pinch Analysis. Point demands associated with these operations are also not considered due to variability in these demands; the quantities involved are however not large. The desuperheater and the pump seals represent further point demands; these operations may only use demineralised water and are excluded from the Pinch Analysis.

5.3.2.3 Final Comments and Problem Statement for the Chemical Production Subsystem

The preceding analysis of the process modules shows that the chemical production subsystem is characterised by a number of demands for materials other than water. As such, there are a number of external sources and sources available within the complex which are used to satisfy these demands. Given the size of the connectivity matrices for the chemical production subsystem (similar to those presented for the demineralisation plant subsystem in Tables 5.2 and 5.3), these are only presented in **Appendix D** alongside the reuse matrix obtained from the optimisation; the reuse matrix shows the mass flows between the various sources and sinks associated with the subsystem.

A few further points related to the modelling of the subsystem are as follows:

- There is a general assumption applied implicitly in the formulation of many of the models for the various process modules which must be pointed out. This assumption is that the model remains representative of the performance of the actual process operation, provided that the inlet concentration constraints are satisfied. Taking an operation which is characterised by a removal ratio as a simple example, this assumption implies that the removal ratio is independent of the concentration in the inlet stream to the process. This assumption may not always be valid practically and the removal of contaminant by the process

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[1] *In the model, these sources were represented with the same concentration profile as demineralised water. It is however noted that this water is unlikely to be as good as demineralised water and some degradation in quality will have occurred through its use. The use of the demineralisation plant as a polishing step for this water may be considered in the final solution.*

operation may depend on the concentration of that contaminant. Some assessment of model validity is therefore required when the results are analysed.

• While the subsystem is optimised in isolation from the other subsystems, allowance still needs to be made for the interactions which exist between the various other subsystems. These interactions include the demand for caustic soda and hydrochloric acid by the demineralisation plant subsystem. Due to there being only one source of concentrated hydrochloric acid, which is further the only source of hydrochloric acid which may be used in the demineralisation plant, this demand is not included in the optimisation model for the chemical production subsystem. Allowance is however made for the caustic soda demand and a demand, representing the daily requirement for caustic soda by the demineralisation plant in its existing configuration, is included in the optimisation model.

• Caustic soda is added to the effluent such that any hydrochloric acid load present in the effluent is neutralised before it is sent to the centralised effluent treatment facility. The sources of hydrochloric acid which become part of the effluent originate from the regeneration procedure of the cation-exchange operation of the brine circuit and the regeneration of the demineralisation plant, both of which are transient activities. The dosage of caustic soda is however continuous and set at a level which would be able to cope with the coincidence of both activities. At present, both basic and acidic effluents from the regeneration procedures are sent to an acid pit in which the two effluents partially neutralise each other. The mixture emerging from the pit remains acidic however, necessitating the neutralisation of the effluent. An improved strategy for this problem might see the complete neutralisation of the effluent at the acid pit, possibly with the routing of other caustic effluents to the pit. Consideration of such a strategy can however only occur once the reuse opportunities for the caustic soda and hydrochloric acid effluents have been investigated. The dosing of caustic soda to the effluent is thus excluded from the Pinch Analysis.

The objective function for the optimisation of the chemical production subsystem may be stated as follows:

The system under consideration comprises the brine circuit and its associated process modules, the caustic evaporation process module, the hydrochloric acid synthesis process module, the sodium hypochlorite synthesis process module, the Hydecat destruction process module, and a number of point sources and demands. Given different material resources, which include water, caustic soda, hydrochloric acid, raw salt, sodium carbonate and sodium bisulphite and other materials such as the flocculant and alpha-cellulose, the task is to identify an optimal network configuration which achieves the required rates of production of chlorine gas, hydrochloric acid and sodium hypochlorite at the

lowest cost. This cost includes the costs associated with the replacement of the cation-exchange resin, the purchase of external sources and the disposal of wastes and effluents produced by the system.

As was the case for the demineralisation plant subsystem, the cost associated with the replacement of the cation-exchange resin is incorporated into the objective function. The form of the objective function for this subsystem is thus identical to that of Equation 5.8. Table 5.7 presents the results obtained from the optimisation problem which was solved using GAMS CONOPT. Further consideration of these results is deferred to **Chapter 6**. The GAMS coding for this model is presented on the **CD** which accompanies this thesis. It should be noted that the figures presented in Table 5.7 represent only those elements of the system included in the optimisation. Elements which were excluded from the Pinch Analysis on the basis of there being no other possible configurations are not represented.

Table 5.7. *Comparison of the water and material requirements and effluent production associated with the existing network configuration and the optimal network configuration for the chemical production subsystem. This comparison only reflects those areas of the subsystem considered in the optimisation.*

	Unit	Existing Configuration	Optimal Configuration
Demineralised Water	[t/d]	198.09	98.64
Umbogintwini River Water	[t/d]	34.62	0
Total Water	[t/d]	232.71	98.64
Raw Salt	[t/d]	142.96	142.71
Hydrochloric Acid (31% m/m HCl)	[t/d]	7.18	6.73
Caustic Soda (32% m/m NaOH)	[t/d]	67.21	66.82
Caustic Soda (38% m/m NaOH)	[t/d]	0	0
Caustic Soda (50% m/m NaOH)	[t/d]	0	0
Sodium Carbonate	[t/d]	1.055	1.061
Sodium Bisulphite	[kg/d]	359.5	353.7
Flocculant	[kg/d]	7.77	8.03
Alpha-Cellulose	[kg/d]	31.08	29.01
Chlorine	[t/d]	14.73	14.72
Steam	[t/d]	70.80	71.67
Effluent	[t/d]	235.19	104.20
Solid Waste	[kg/d]	39.86	37.63
NaCl Load to Effluent	[t/d]	14.2	13.73
NaOH Load to Effluent	[kg/d]	39.9	84.0
Duration of Normal Cycle of Operation of Cation-Exchanger	[h]	72	72.56

5.3.3 The Cooling Circuit Subsystem

The cooling circuit subsystem comprises the four cooling towers and their associated cooling circuits located on the chlor-alkali complex, that is, the Linde, Sulzer, LC and MBC cooling circuits. The Linde and Sulzer cooling circuits are associated with the liquefaction of chlorine while the LC and MBC cooling circuits meet the cooling requirements associated with the use of liquefied chlorine and the brine circuit respectively. In optimising this subsystem, thermal effects are not considered and the assumption is made that the necessary cooling requirements of the complex can be met if the flowrates to the various cooling towers are maintained at their current levels.

The subsystem comprises four process modules representing each of the cooling towers and their associated cooling circuits. With the mathematical models being identical for all the cooling towers, the process module is considered generally in the following discussion. The mathematical description of these models is presented in the GAMS coding presented on the **CD** accompanying this thesis.

With regard to the formulation of a model to represent the operation of the cooling towers, two effects are noted. Firstly, there is the evaporation of water from the cooling tower which concentrates the dissolved species present in the water. The second effect is the absorption of carbon dioxide from the atmosphere which increases the carbonate concentration in the water. With plant data collected for the cooling circuit subsystem not being conclusive on its own, simulation was required in conjunction with this data in deriving models for the various cooling towers. Here, the assumption was made that no dissolved solids are removed by the evaporation process. The absorption of carbon dioxide from the atmosphere by the water was then approximated by the addition of a mass-load of Na_2CO_3. This quantity was derived from the equilibrium concentration of carbonate in the water (following evaporation) in contact with the atmosphere, as determined using the aquatic speciation software package MINTEQA2 (Allison et al., 1991). It was assumed that this mass-load addition was independent of concentration in the concentration range considered by the optimisation.

The process module for each cooling tower has a single water demand and a single water source associated with it. Constraints specifying blowdown volumes are not included in the models for the process modules since these are determined during the course of the optimisation and subject to the inlet concentration limits of the cooling towers (which are maintained at their existing concentrations initially). With the cooling towers only using water, it is not necessary to represent all species presented in Table 5.1 in the model. One significant measure for cooling circuits which is however included in the model is the total dissolved solids (TDS) present in the water. As has already been noted, this measure is a composite concentration indicator. Since it includes the species NaCl, Na_2SO_4, Na_2CO_3, $CaCl_2$ and $MgCl_2$ its value is not independent of these constituent species. Thus, in modelling this composite species, attention must be given to ensuring that mass-load additions of the constituent species are also accounted for in the TDS balances.

In considering the optimisation of the cooling circuit subsystem in isolation from the other subsystems, only the water sources presently available to the subsystem are considered in the optimisation. Any water sources currently used by the other subsystems but not used in the optimised scenarios are considered unavailable to the cooling circuit subsystem at this stage. The objective function for the optimisation of the cooling circuit subsystem may thus be stated as follows:

> *The system comprises process modules representing the four cooling towers located on the chlor-alkali complex and their associated cooling circuits. Given a single external source of water, the task is to identify an optimal network configuration which is able to supply sufficient water to each of the cooling towers, subject to the associated quality constraints, at minimum cost. This cost includes the costs associated with the purchase of the water and the disposal of the blowdown effluent produced by the subsystem. Thermal effects are not considered in the optimisation.*

The objective function for this problem corresponds to Equation 4.12. The model is solved using GAMS CONOPT. Table 5.8 presents the comparison between the results obtained from the optimisation problem and the current operating scenario while Figure 5.10 presents the proposed network configuration for the cooling circuit subsystem. These results are considered in greater detail in **Chapter 6**.

Table 5.8. *Comparison of the water requirement and effluent production associated with the existing network configuration and the optimal network configuration for the cooling circuit subsystem.*

	Unit	Existing Configuration	Optimal Configuration
Umbogintwini River Water	[t/d]	846.62	828.16
Effluent	[t/d]	128.12	109.66
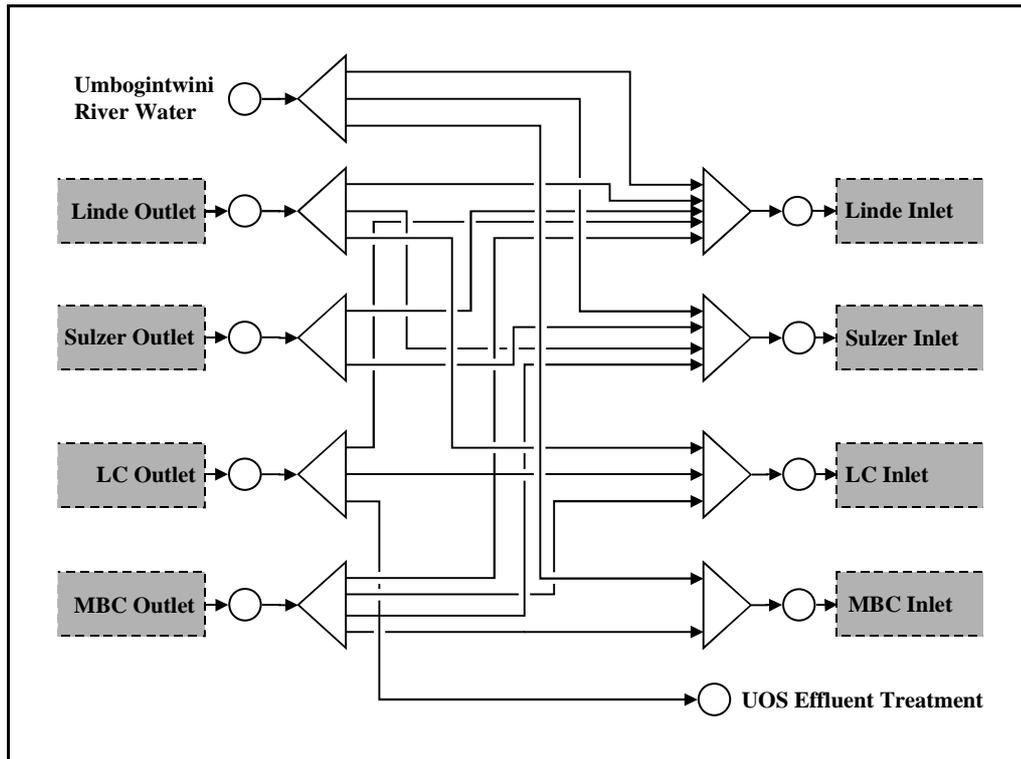
Figure 5.10. *Diagram showing the optimal network configuration for the cooling circuit subsystem.*

5.4 SOME GENERAL POINTS ON MODELLING AND OPTIMISATION

With the subsystems described in the preceding section representing complex optimisation problems, it is deemed appropriate to make a few general notes regarding the modelling and optimisation of these subsystems.

Firstly, as has already been established, the models for the subsystems are nonlinear and contain bilinear terms. In solving these problems, standard optimisation tools may experience difficulty in finding feasible solutions. In addition, there are no guarantees that the solution produced by the optimisation tool is globally optimal.

In dealing with the first issue, it must be certain that a feasible solution does indeed exist within the formulated superstructure. Since it is known that the existing configuration represents a feasible network configuration, the superstructure must include this configuration as a possibility. In addition, sources which are known to satisfy the inlet requirements of the process modules, and sinks which are guaranteed to accept any flow from sources within the superstructure are included in the model so that a feasible solution should always be possible. These sources and sinks are of an artificial nature however and only have meaning in the model, that is, there is no physical equivalent to these sources and sinks. For this reason, these sources and sinks have higher cost factors associated with them such that the optimisation algorithm, which in this case seeks to minimise the operating cost of the network, should

favour the use of the cheaper sources and sinks which correspond to those with physical meaning. The inclusion of the artificial sources and sinks in the optimisation problem serves as a check on the performance of the optimisation algorithm and a troubleshooting tool for locating mistakes made in the modelling. Should these sources and sinks be used in the solution produced by optimisation algorithm then either the algorithm has not reached the optimal value or there is some factor present in the model which forces the use of these artificial sources and sinks.

The provision of a suitable set of initial values for the variables of the model to the optimisation algorithm is critical to the convergence of the model to a feasible solution. In addition, the chances of the feasible solution coinciding with the global optimum is enhanced if this set of values corresponds to a feasible solution in the vicinity of the global optimum. For this problem, a feasible solution corresponds to a feasible network structure and the corresponding material flowrates associated with this structure. Thus, the initial feasible solution provided to the optimisation algorithm in this study corresponds to the existing network configuration. A combination of artificial sources and real sources are used in the process modules in this initial solution while materials from the process modules are discharged to a combination of real and artificial sinks in the superstructure.

Having considered the provision of an initial feasible solution to the algorithm, consideration now turns to the solution produced by the optimisation algorithm and in particular whether or not the solution is globally optimal. This study does not utilise rigorous global optimisation and relies on the use of the standard optimisation algorithms. It is noted that the provision of different initial feasible solutions improves the chances of locating the global optimum and this is the strategy which has been used in this study.

As a final word, some problems were encountered in achieving convergence on the model, especially for the chemical production subsystem. These problems were overcome by excluding some of the mixed-integer constraints from the model. With the solution provided being satisfactory, no further effort was directed in overcoming this problem.

5.5 CONCLUDING REMARKS

In terms of the objectives of this study, **Chapter 5** has considered the application of the Combined Water and Materials Pinch Analysis methodology to the chlor-alkali complex. Given the complexity and size of the problem presented by the chlor-alkali system, the system was divided into three smaller subsystems, each of which was made of one or more process modules. The modelling of these subsystems and process modules was presented and the more important modelling assumptions highlighted. While an impression of the results obtained from the optimisation of the subsystems in isolation from each other was provided in this chapter, no analysis of these results was presented; this is the focus of **Chapter 6**.

5.6 CHAPTER REFERENCES

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6

ANALYSIS OF RESULTS

There are two important positive attributes associated with the application of Pinch Analysis in comparison to "just optimisation". The first of these is that it provides strategies as to how resources should be used such that they are used to their maximum potential. The second attribute is that once these strategies have been identified, insight is provided as to what interventions can be effected to the system such that further improvement in the efficiency of use may be achieved. This chapter considers the results obtained from the optimisation in terms of these two attributes. Before this is done however, the significance of the pinch as it pertains to Combined Water and Materials Pinch Analysis is considered, as is the approach to identifying suitable process interventions which may be effected to the system; these considerations are presented in Section 6.1. Section 6.2 considers the results from the optimisation of the various subsystems in isolation from each other while Section 6.3 considers the strategy required for the integration of the subsystems and the results obtained from this integration. Section 6.4 presents a comparison of the results obtained from the three different Water Pinch Analysis studies carried out at the chlor-alkali complex, that is, the initial Water Pinch Analysis study conducted by Gardner (Gardner, 1999), the simplified Water Pinch Analysis study for which results are presented in Appendix B, and this, the Combined Water and Materials Pinch Analysis study. Given that the Umbogintwini complex is no longer operational, some consideration is given to the continuation of the study on other chlor-alkali complexes in Section 6.5. Concluding remarks on this chapter are presented in Section 6.6.

6.1 THE SIGNIFICANCE OF THE PINCH FOR COMBINED WATER AND MATERIALS PINCH ANALYSIS

The first applications of Pinch Analysis occurred in the area of heat integration in the late 1970s (Linnhoff and Flower, 1978). With the application of this technique to a system comprising hot streams requiring cooling and cold streams requiring heating, the identification of the pinch point for the system served as an indication that the maximum level of heat integration between the two sets of streams had been achieved. The pinch point further served as a significant point around which a design procedure was developed such that a network of

heat-exchangers, achieving the predicted level of heat integration, could be realised. In this context the pinch point corresponds to a temperature. Above this temperature, the system has a heating demand which must be satisfied by utility heating while below this temperature, the system has a cooling demand which must be satisfied by utility cooling. The pinch point, together with composite curves, which provide a graphical representation of the performance of the system, thus direct attention to interventions which could bring about further improvement in the performance of the system. Such interventions involve measures which reduce the heating and cooling demands above and below the pinch temperature respectively.

Since this initial application of Pinch Analysis, the approach has been applied to other areas of process synthesis, a review of which is provided by Linnhoff (1993). Pinch points have been identified and composite curves constructed to provide global insight into the performance of the systems that these extensions consider. Many of these extensions however use mathematical programming. In most cases, mathematical programming achieves the targeting and design steps simultaneously. The identification of the pinch point is therefore not needed for design purposes. However, from the perspective of gaining insight into the system, the identification of the pinch point remains a key element in reported studies. Effort is therefore expended on the identification of the pinch point from the solution provided by the optimisation algorithm.

In terms of the field of water-reuse network design, several researchers have given consideration to the pinch point as it pertains to systems in which water-use is minimised amongst a set of processes. Wang and Smith (1994) interpret the pinch point for the system of water-using mass-exchange operations as the concentration at which the water supply line touches the limiting composite curve on a plot of contaminant concentration versus mass-load removed. Oleson and Polley (1997) consider the pinch point as a significant concentration relative to which process operations should be placed in achieving a network design which meets the predicted target. In terms of the Two-Composite methodology, Dhole et al. (1996) define the pinch point as the point where the source and demand composite curves touch one another. As such, the range over which the source and demand composite curves overlap, which is representative of the level of reuse in the system, is limited by the pinch point. Sorin and Bédard (1999) comment that the Two-Composite methodology produces a number of local pinch points where the source and demand composite curves touch each other and that this leads to an obscuring of the concept of the pinch point. The global pinch point is introduced by these authors to provide consistency between the pinch point defined by Wang and Smith (1994) and the pinch point defined by Dhole et al. (1996). The global pinch point corresponds to the species concentration of the purest source for which a portion is diverted to effluent without there being an increase in the freshwater consumption by the system. Other researchers identify two different pinch points. Kuo and Smith (1998) identify both freshwater and regeneration pinch points, as do Castro et al. (1999) and Mann and Liu (1999). Mann and Liu (1999) identify two pinches associated with the Two-Composite Plot of Dhole et al. (1996), namely the freshwater pinch and the reuse pinch. Both pinches are defined in terms of a vertical flowrate line on the Two-Composite Plot; the freshwater pinch represents the borderline between the freshwater-use and water-reuse regions of the diagram while the reuse

pinch represents the boundary between the water-reuse region and the wastewater production region of the diagram.

As a general comment on the interpretations of the pinch point presented by these researchers, it is noted that the pinch is a mass-transfer or mass-balance concept. As it has been used here, it identifies a thermodynamic limit for the set of process operations under consideration. As such, it is a thermodynamic limit which prevents a further reduction in the amount of freshwater used by the system. For systems involving only a single contaminant, it is possible to identify the pinch point using a graphical approach, as has been shown by these researchers. This is because the optimisation problem is 1-dimensional. When the system involves more than one contaminant, the optimisation problem becomes multidimensional and the identification of the pinch point is more difficult using a graphical approach. In addressing this problem Wang and Smith (1994) introduced a concentration shifting procedure such that it is possible to identify the pinch point for a system involving multiple contaminants using a graphical approach. Essentially, this shifting procedure identifies a locus along which the optimisation problem appears 1-dimensional, which is of course the basis of the graphical approach.

A further characteristic of this approach is that the problem considered by these researchers involves the minimisation of a single freshwater resource. With only a single source available, minimising the amount of freshwater used simultaneously minimises the economic cost. The thermodynamic minimum amount of water used by the system therefore coincides with the economic minimum. While multiple sources of freshwater were considered by Wang and Smith (1995), the incorporation of the different costs associated with these sources remained implicit.

The problems considered by these researchers further involve only non-reactive contaminants. While it may be possible to develop some kind of shifting procedure involving the reactive species, such that a locus is identified from which the optimisation problem appears 1-dimensional, it is likely that this approach will break down where multiple resources are involved, if only because there is a problem in trying to weight the contributions from the different resources. While some thermodynamic weighting system might exist, it has not been identified as yet. There is further uncertainty in the usefulness of such a weighting system, given that the motivation for this type of problem would most likely involve the minimisation of cost.

Given the limitations of the graphical approach noted here and previously, mathematical programming allows problems involving multiple species and multiple resources to be solved. Constraints such as enforced and forbidden matches between process operations and minimum flowrates through process operations may be incorporated into the problem and a larger variety of process operations can be considered. In terms of providing a weighting system to represent the relative significance of the different resources in the problem, economic cost may be used, although other weighting systems, such as environmental impact or the suggested thermodynamic weighting system, could also be used. Given these considerations however, a question arises as to how the pinch should be interpreted in this situation. As such, economic

considerations may lead to a design optimum which does not observe the pinch restrictions of no-cross pinch use of a resource. The reuse of resources may further be limited by an enforced match or a minimum flowrate to an operation; the nature of the pinch is thus no longer thermodynamically based.

The answer to this question is provided by Linnhoff et al. (1994a) in their consideration of the insight provided by Pinch Analysis into the performance of the system under consideration. In terms of the identification of process interventions in the context of energy integration, these authors comment that the nature of Pinch Analysis as a systematic approach will leave the practitioner feeling constrained to fixed flows and temperatures. However, they proceed to argue that critical areas of the system are identified and lateral thinking stimulated such that process modifications to these areas may be proposed. They point out that such modifications represent fundamental changes in the input data for the problem; the problem should thus be re-solved to justify the merits of the proposed interventions.

From this discussion, the pinch provides insight into the critical areas of the problem to which process interventions should be effected, such that the performance of the system may be improved. Relating these ideas back to the pinch, it is these areas of the problem which give rise to the pinch and constrain the performance of the system. These areas are described by mathematical constraints in the model and as such the pinch relates to the constraint or set of constraints which limits the performance of the system. In the energy integration sense, the performance of the system is measured in terms of the amount of energy recovery taking place between the set of hot streams and the set of cold streams.

These concepts are of course not specific to the energy integration problem. In terms of the Combined Water and Materials Pinch Analysis problem, the pinch is similarly defined as the particular constraint or set of constraints which limits the performance of the system. For the Combined Water and Materials Pinch Analysis problem, this performance is measured in terms of the cost of resources. This definition is thus a departure from the conventional interpretation of the pinch which has a thermodynamic basis. In addition, this definition relates the pinch to a constraint or set of constraints rather than a point.

In terms of the identification of process interventions for water-reuse networks, the literature contains two main approaches, both of which are derived from the solution provided by mathematical programming. It is a trend of at least two of the commercially available water-reuse network design packages to construct composite curves from the data provided by the optimisation algorithm (Dhole et al., 1996; Tainsh and Rudman, 1999; Koufos and Retsina, 2000). These composite curves correspond to those of the Two-Composite methodology and for problems involving multiple contaminants, the curves are plotted separately for each contaminant. Doyle and Smith (1997) propose a methodology for the construction of a composite curve for a system of mass-exchange type operations involving multiple contaminants from the solution provided by an optimisation algorithm. A shifting procedure similar to that proposed by Wang and Smith (1994) is used to account for the multiple contaminant nature of the problem. It is noted by these authors that the construction includes flow and forbidden match constraints in addition to concentration constraints.

While this statement does apply to both cases in that these constraints are incorporated into the mathematical programming problem, the composite curves do not provide complete insight into why the pinch arises. In plotting the solution on concentration versus water flow axes, only the contaminant concentration constraints are represented. The pinch, as it is defined above, may however result from an enforced match or may be due to a minimum flowrate requirement constraint associated with some operation in the process system. These constraints are however not explicitly evident from the concentration composite curves.

The second approach for identifying process interventions for water-reuse networks is the use of the marginal values which are available from the solution provided by the mathematical programming software. These measures identify which are the most significant constraints in the problem and provide an indication of what the incentives are if these constraints are relaxed (Rossiter and Nath, 1995). The use of these values as a means of identifying process interventions is noted by Mann and Liu (1999) and implemented in the WaterPinch™ software (Linnhoff March Limited, 2001). Some insight into these values is now provided.

The set of constraints associated with an optimisation problem is divided into a set of equality constraints and a set of inequality constraints. The inequality constraints are of the form:

$$g(x) \leq 0$$
6.1

where $g(x)$ is an arbitrary constraint and x represents the set of variables adjusted during the course of the optimisation. When the left-hand side of Equation 6.1 is equal to the right-hand side, that is, the equality is active, the objective variable in a minimisation problem will be prevented from decreasing further by this constraint. As such, there is a sensitivity associated with the objective variable with respect to this (equality) constraint and the marginal value associated with this constraint is a manifestation of this sensitivity.

The constraint functions $g(x)$ will have parameters which are considered as constant during the optimisation. The marginal value associated with a constraint provides a quantification of the effect on the objective variable should one of the constants within the constraint equation change by an infinitesimal amount. Mathematically, should the (equality) constraint $g(x)$ change by an infinitesimal amount ε such that:

$$g(x)\text{-}\varepsilon = 0$$
6.2

then the marginal value λ associated with the constraint corresponds to:

$$\frac{\partial Z}{\partial \varepsilon} = \lambda$$
6.3

where Z is the constrained objective function for the problem as evaluated at the optimum. The derivation of Equation 6.3 is part of basic optimisation theory and is available in standard optimisation texts such as Wilde and Beightler (1967) and Edgar et al. (2001).

Marginal values are reported for all active constraints, that is, equalities and inequalities which have reached their bounds. Marginal values thus represent the sensitivity of the system to all constraints rather than only certain constraints, for example, concentration constraints. As such they direct attention to those areas of the system for which interventions will have the greatest impact. Unfortunately they are only valid in a very limited range around the current optimal point and there is no indication as to the size of this range. In terms of the definition of the pinch, it will be a particular constraint or set of constraints which prevents a further reduction in the cost associated with the system. In relaxing these constraints, that is, adjusting their values such that they become less restrictive, a point will be reached where another constraint or set of constraints becomes active. This constraint or set of constraints corresponds to a new pinch and different marginal values will be reported by the optimisation algorithm for this set of active constraints.

The marginal value reported for a constraint which has reached its bound is applicable to a perturbation in any one of the constant parameters present in the constraint. The source of these constants in the system may correspond to certain physical limits, for example, non-negativity constraints, or some other characteristics related to the physical design of the process equipment, for example, capacity limits. Excluding the possibility that there is any uncertainty in these parameters, which could of course be rectified by obtaining a more accurate measurement of the parameter, it is noted that it may be impossible, or at least very difficult or expensive, to effect process interventions which bring about a change in the value of these constants. Other constants however are not based on any physical boundaries. For example, the species concentration limits arise due to considerations of feasible operation rather than some absolute limitation. As such, these constants are more easily adjusted through process interventions. In addition, where species concentration limits are concerned, careful consideration is required in assessing the validity of existing limits.

As an illustration of these concepts, the example of a system of mass-exchange operations of the type considered by Wang and Smith (1994) is used. For this system of operations, the set of pinch constraints will include a concentration limit associated with the inlet or outlet of one of the mass-exchange operations. This operation is described in terms of a fixed mass-load addition as shown in Equation 6.4:

$$\Delta m = F_w \cdot (C_w^{out} - C_w^{in}) \qquad\qquad 6.4$$

where Δm is the mass-load of contaminant transferred from the process stream to the water stream in a particular operation, F_w is the water flowrate through that operation, and C_w^{in} and C_w^{out} are the contaminant concentrations at the inlet and outlet to the operation respectively. In this situation, the pinch arises due to a combination of these factors rather than only the

concentration limits, only the flowrate through the operation or only the mass-load of contaminant transferred to the water stream. Thus, in identifying interventions which will reduce the flowrate target of the network, an intervention which achieves an adjustment to any one of these variables may be effective in reducing the water demand of the process; some factors are of course more easily adjusted than others. It is however noted that all variables cannot vary independently since they are related by Equation 6.4.

The problem at hand seeks to minimise the cost associated with the use of a range of resources and the disposal of effluents generated during the use of these resources. Given the variety of constraints associated with the problem, the use of information derived from the marginal values is favoured in identifying the significant areas of the problem which should be explored as candidates for process interventions. Graphical constructions in the form of composite curves may still yield useful information, though this possibility is not explored here.

6.2 SUBSYSTEM OPTIMISATION RESULTS

This section considers the results obtained from the optimisation of each of the subsystems described in **Chapter 5**; these results correspond to those obtained from the optimisation of the subsystems in isolation from each other. In these optimisation models, allowance for the interactions which exist between the subsystems is made by the addition of constraints which guarantee that the optimised subsystem will meet the requirements of the other non-optimised subsystems as they exist in the present configuration.

It was noted in **Chapter 5** that this type of study involves a large number of assumptions which must be made such that a simple representation can be achieved for an otherwise complicated system. While only the more significant assumptions were highlighted in the discussion on the formulation of the subsystem models, even these represent a large number. From a scientific perspective, the results from the study should be analysed in terms of the assumptions made, such that the significance of the results can be understood completely. However, given the large number of assumptions involved, it is not considered practical to assess the impact of each assumption on the results. Moreover, it is not considered to be the primary focus of this study which is concerned more with the development and demonstration of the Combined Water and Materials Pinch Analysis methodology. The significance and validity of the results will therefore be considered in a more general sense.

The presentation of results from the optimisation of the subsystems in isolation from each other is as follows: **Section 6.2.1** presents the results obtained for the demineralisation plant subsystem; **Section 6.2.2** presents the results obtained for the chemical production subsystem; and, **Section 6.2.3** presents the results obtained for the cooling circuit subsystem.

6.2.1 The Demineralisation Plant Subsystem

Figure 6.1 represents the proposed network configuration for the demineralisation plant subsystem as provided by the optimisation algorithm. The reuse matrix for the demineralisation plant subsystem, which shows the mass flows between the various sources and sinks associated with the subsystem is presented in **Appendix D**; other results may be found on the **CD** which accompanies this thesis. This section presents the results from the optimisation of the demineralisation plant subsystem in isolation from the other subsystems as follows: **Section 6.2.1.1** considers the significant features of the proposed solution; **Section 6.2.1.2** presents considerations related to the implementation of the proposed solution; and, **Section 6.2.1.3** presents an analysis of the marginal values provided by the optimisation such that areas for improvement in the model or process interventions which bring about further improvement in the performance of the subsystem may be identified; consideration of the validity of the results is presented in this section.
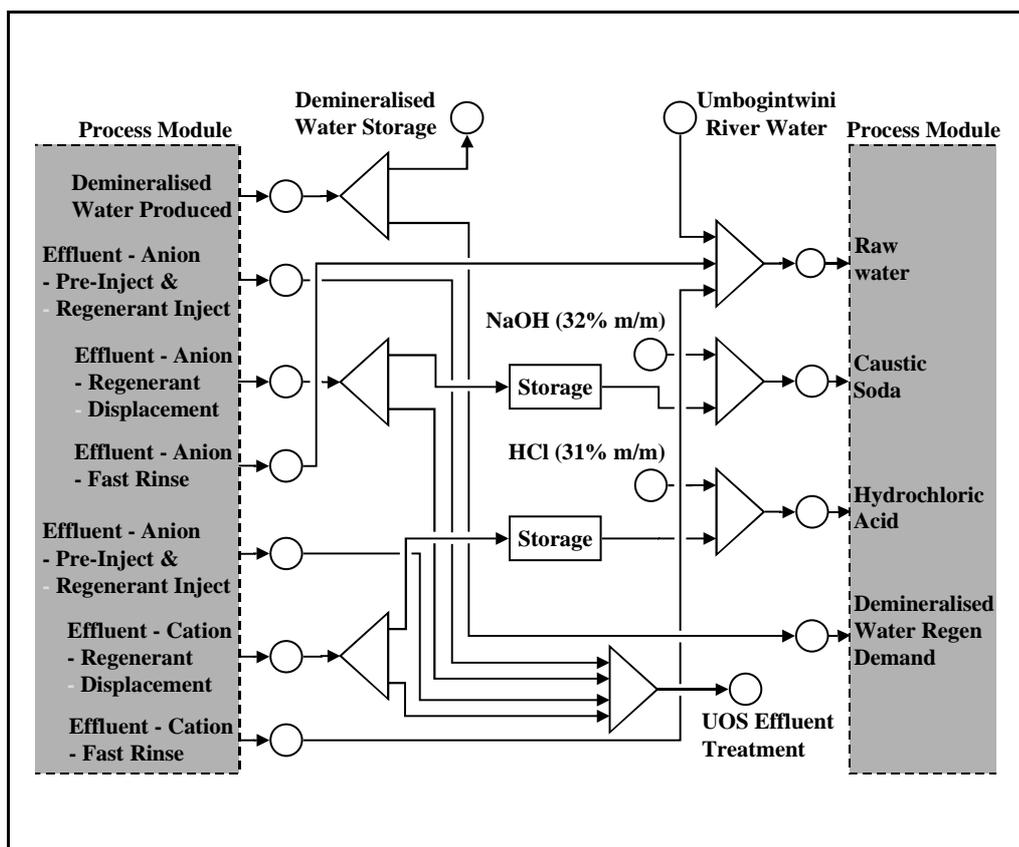
Figure 6.1. *Diagram showing the optimal network configuration for the demineralisation plant subsystem.*

6.2.1.1 *Features of the Optimal Configuration for the Demineralisation Plant Subsystem*

The notable features of the solution from the optimisation of the demineralisation plant subsystem are summarised as follows:

- Only Umbogintwini River water is used in the production of demineralised water

- A portion of the NaOH-containing effluent from the Regenerant Displacement stage of the anion regeneration is used in the preparation of the dilute caustic soda required for the subsequent regeneration cycle. A similar reuse strategy applies for the HCl-containing effluent from the Regenerant Displacement stage of the cation regeneration.

- Effluent from the Fast Rinse stages of the cation and anion regenerations is recovered completely and used in the production of demineralised water.

Table 6.1[1] presents a comparison between the performance of the demineralisation plant in its existing configuration and the configuration proposed by the solution of the optimisation model for the production of a fixed quantity of water. Significantly, there is a substantial increase in the frequency of regeneration of the demineralisation plant and approximately six regeneration cycles are required in the optimal configuration to every five in the existing configuration. This increase is due to the exclusive use of the Umbogintwini River water rather than the blend of Umgeni Water and Umbogintwini River water. This indicates that the costs associated with the increased regeneration frequency are offset by the savings accrued through the use of the less expensive, but more contaminated, water source.

In addition to the increase in regeneration frequency, there are increases in the amounts of caustic soda and hydrochloric acid required in the production of the fixed quantity of demineralised water. However, the quantity of water required for this production and the effluent associated with this production are reduced. The NaCl load associated with the effluent does however show a slight increase. Significantly, the proportion of the total demineralised water production available to the rest of the plant has increased in the optimal configuration; a smaller proportion of the water treated by the demineralisation plant is used for regeneration purposes, despite the increase in regeneration frequency.

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[1] *As a general comment on the data presented in the various tables in this thesis, and in particular in this chapter, it is noted that the number of significant figures reported may not always be consistent with what is scientifically meaningful. The reported number of significant figures is chosen to illustrate differences in the comparisons which are drawn and are derived from computer modelling. It is left up to the reader to judge the level of significance which should be attached to these figures.*

Table 6.1. *Comparison of water and material requirements and effluent production associated with the existing network configuration and the optimal network configuration. A fixed amount of demineralised water is produced by both configurations.*

	Unit	Existing Configuration	Optimal Configuration
Demineralised Water Produced	[t]	254.87	254.87
Number of Regeneration Cycles	[ ]	1	1.22
Umbogintwini River Water	[t]	130.45	254.93
Umgeni Water	[t]	130.45	0
Total Water	[t]	260.90	254.93
Hydrochloric Acid (31% m/m HCl)	[kg]	350.00	366.42
Caustic Soda (32% m/m NaOH)	[kg]	390.00	407.70
Caustic Soda (38% m/m NaOH)	[kg]	0	0
Caustic Soda (50% m/m NaOH)	[kg]	0	0
Demineralised Water Available to Other Subsystems	[t]	239.20	241.18
Effluent	[t]	22.42	14.51
NaCl Load to Effluent	[kg]	195.13	202.64

Table 6.2 presents a comparison between a single cycle of operation for the existing configuration and the optimal configuration of the demineralisation plant. These figures show that the quantity of water that the demineralisation plant is able to process during a single cycle of operation is substantially lower for the demineralisation plant in its optimal configuration. This is consistent with the exclusive use of Umbogintwini River water; the exchange capacity of the demineralisation plant is reached more rapidly due to the greater ionic load associated with this water in comparison to that of Umgeni Water.

It has been observed already that in the purification of a fixed quantity of water by the demineralisation plant, a greater proportion of the water is available to the rest of the plant in the optimal configuration compared to the existing configuration. It is clearly this quantity, that is, the proportion of water available to the plant, which is of interest since the demineralisation plant's function is to supply high purity water to the rest of the plant. Thus, a comparison is drawn, projected over an annual period (360 days), between the performance of the existing configuration and the optimal configuration. The criteria for this comparison is that the amount of water made available to the rest of the plant be at the level provided by the existing configuration. Table 6.3 presents the results from this comparison.

Table 6.2. *Comparison between a single cycle of operation of the demineralisation plant in its existing configuration and the proposed optimal configuration.*

	Unit	Existing Configuration	Optimal Configuration
Duration of Normal Cycle of Operation	[h]	16.00	12.68
Umgeni Water	[t]	130.45	0
Umbogintwini River Water	[t]	130.45	209.07
Total Water	[t]	260.90	209.07
Demineralised Water Produced	[t]	254.87	209.02
Demineralised Water Available to Rest of Plant	[t]	239.20	197.79
Hydrochloric Acid (31% m/m HCl)	[t]	0.350	0.300
Caustic Soda (32% m/m NaOH)	[t]	0.390	0.334
Effluent	[t]	22.42	11.90

Table 6.3. *Comparison of the performance of the demineralisation plant in its existing configuration and the proposed optimal configuration as projected over an annual period (360 days). The comparison is based on a fixed amount of demineralised water being available to the rest of the plant.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Demineralised Water Requirement by Rest of Plant	[t/y]	107 733	107 733	0
Regeneration Cycles	[cycles/y]	450	545	-21
Umgeni Water	[t/y]	57 407	0	-
Umbogintwini River Water	[t/y]	57 407	113 876	-
Total Water	[t/y]	114 814	113 876	0.8
Hydrochloric Acid (31% m/m HCl)	[t/y]	158	164	-3.8
Caustic Soda (32% m/m NaOH)	[t/y]	176	182	-3.7
Effluent	[t/y]	10 100	6 481	36
Total Cost*	[R/y]	540 667	441 653	18
NaCl Load to Effluent	[t/y]	87.9	90.5	-3.0
NaOH Load to Effluent	[t/y]	0.99	0.94	4.7
Total Demineralised Water Production	[t/y]	114 793	113 849	0.8
Unit Cost of Demineralised Water*	[R/t]	4.71	3.88	18

* *These costs correspond to those for the year 2000.*

Similar trends to those observed in the preceding tables are observed in Table 6.3. Notably, an additional 95 regeneration cycles occur over this period in the optimal configuration. With a greater proportion of the total production of demineralised water being available to the plant in the optimal configuration, the total quantity of demineralised water produced by the plant in this configuration is slightly lower than that of the existing configuration. Further points of note are the 36% reduction in the quantity of effluent produced by the optimal configuration and the 18% reduction in the overall operating cost. This reduction sees a decrease in the unit cost associated with demineralised water from R 4.71 per ton to R 3.88 per ton.

6.2.1.2 *Implementation Considerations for the Demineralisation Plant Subsystem*

Having presented the significant features of the solution proposed by the optimisation, attention shifts to the implications involved in implementing the proposed solution. Clearly the substitution of Umgeni Water with Umbogintwini River water is easily handled. In terms of the other modifications, the following points are noted:

- The reuse of effluent from the Regenerant Displacement stage of the regeneration procedure in the preparation of the regenerants (reagents) for the subsequent regeneration cycle requires storage capacity. The necessary storage capacity is already available in the regenerant mixing tanks associated with the demineralisation plant.

- The recovery of water from the Fast Rinse stage to the normal cycle of operation of the demineralisation plant involves a small change in the regeneration control strategy. Water is presently recycled from the Quality Rinse stage to the normal cycle of operation. Hence, with the necessary piping already in place to achieve this part of the proposed configuration, only the stage in the regeneration procedure at which the recycle begins must be altered.

From these considerations, the implementation of the proposed reuse strategy involves only minor process changes.

6.2.1.3 *Demineralisation Plant Subsystem Solution Analysis*

This section analyses the solution for the demineralisation plant subsystem in terms of the marginal values provided by the optimisation. Based on this analysis, areas of the model which could be improved, and process interventions which could bring further improvement in the performance of the subsystem are identified. Marginal values are reported for all active constraints, that is, equalities and inequalities that have reached their bounds. These constraints limit the performance of the system and are responsible for the pinch.

If it is assumed that all the parameters associated with the design and performance of the demineralisation plant and the regeneration procedure are correct, that is, that the model for the subsystem is representative of the actual design and performance of the operations concerned, then the sensitivities (marginal values) reported by the optimisation algorithm must correspond to the quantity and the quality associated with the raw water being treated by the plant. If it is assumed further that the quantity of water processed by the plant is unable to change, then the sensitivities arise purely from the quality of the water entering the plant. Figure 6.2 presents a graphical representation of the sensitivities associated with each of the species at the raw water inlet to the demineralisation plant. These sensitivities represent the economic saving per unit change in the mass fraction of the species in the influent water.
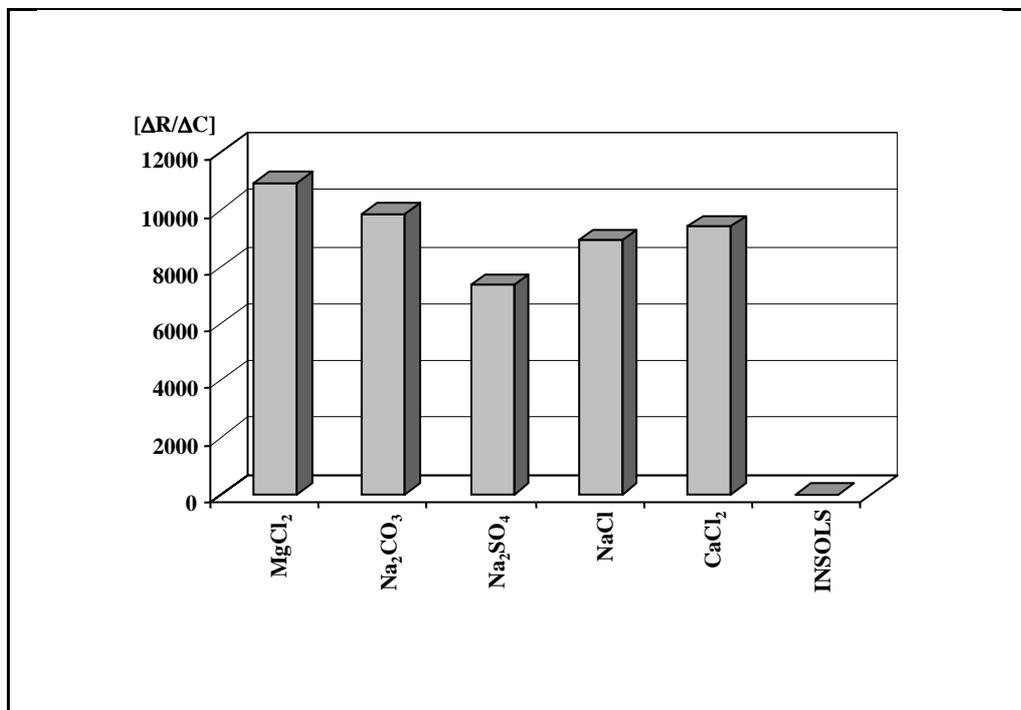
Figure 6.2. *Graphical representation of the non-zero marginal values associated with the concentrations of the different species at the inlet to the demineralisation plant. Concentration is expressed in terms of mass fraction.*

While the marginal values associated with the concentrations of the various species are different, these marginal values all translate to a single sensitivity value of the cost to the ionic load associated with the water entering the demineralisation plant. The coincidence of these values stems from the assumption that all species compete equally for any exchange-site associated with the ion-exchange resin. As a comment on the validity of this assumption, it is noted that divalent ions, for example, would compete more strongly than monovalent ions. An improvement to the model addressing this issue may thus be appropriate.

Figure 6.3 shows the sensitivities reported for the concentration limits for the material inlets associated with the regeneration sequence. Non-zero marginal values only exist for the hydrochloric acid and caustic soda inlets to the regeneration procedure. As such, Figure 6.3 indicates a sensitivity of approximately 17.77 Rand per 0.01 relaxation in the mass fraction limit of HCl at the hydrochloric acid inlet and a sensitivity of 7.77 Rand per 0.01 relaxation in the mass fraction limit of NaOH at the caustic soda inlet; in both cases, a 0.01 relaxation in the mass fraction limit corresponds to a reduction of approximately 1% m/m in the strength of the regenerants used for regeneration. Assuming however that the concentration limits for these species are at their correct values and cannot be relaxed, a closer examination of the sources used in meeting these demands is appropriate.
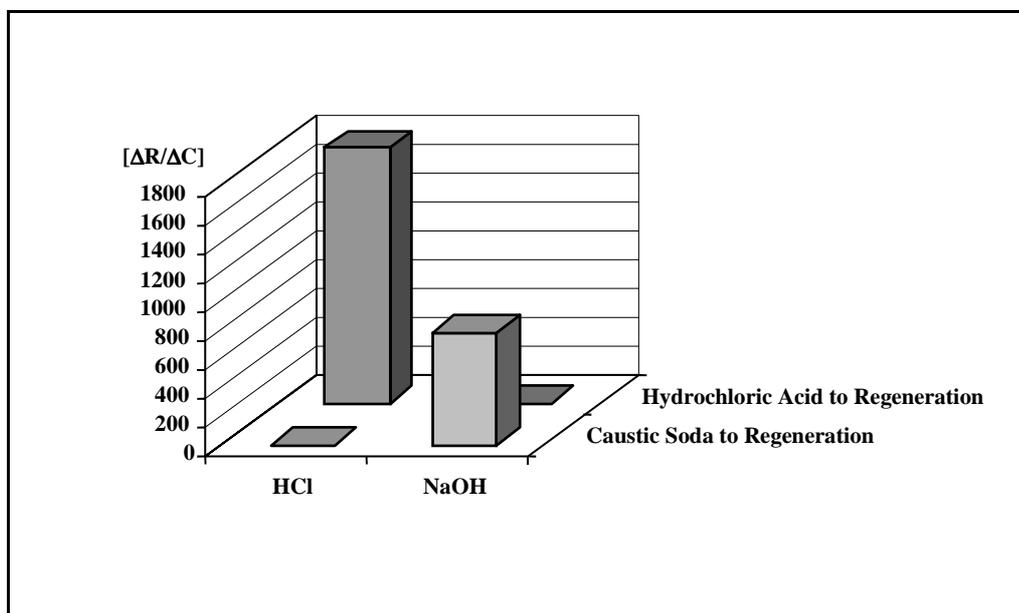
Figure 6.3. *Graphical representation of the non-zero marginal values associated with the concentration limits of the different species at the inlets associated with the regeneration sequence of the demineralisation plant. Concentration is expressed in terms of mass fraction.*

From an examination of the solution provided by the optimisation algorithm, only a portion of the effluent generated from the Regenerant Displacement stage is used in the preparation of the regenerant required for the succeeding regeneration cycle. Associated with the demand for the regenerant is both a flowrate equality constraint and a minimum regenerant species concentration constraint, which becomes binding due to the economic value of the regenerant. The concentration of the regenerant species in the effluent from the Regenerant Displacement stage is however too low to meet the regenerant load requirement and the use of the concentrated regenerant source is required to make up the deficit. The concentration of the regenerant species in the effluent from the Regenerant Displacement stage is also not high enough to allow the entire volume of the effluent to be reused.

In formulating the model for the demineralisation plant process module, the assumption was made that the effluents from each stage are uniformly mixed. Due to the way in which the model was formulated, this assumption applied to the entire volume of effluent associated with a particular stage. This is consistent with the entire volume of effluent from that stage being collected before any reuse takes place. In terms of the Regenerant Displacement stage of the regeneration sequence, the resin bed contains only regenerant at the start of the stage. When demineralised water begins to enter the resin bed, displacing the regenerant, the effluent which emerges from the bed has the characteristics of the regenerant. As the stage progresses, the effluent gradually changes such that it has the characteristics of demineralised water. In collecting the effluent emerging from the Regenerant Displacement stage, the regenerant species concentration in the effluent decreases as more effluent of demineralised water quality is added. The assumption applied in the model, that the entire volume of effluent is considered uniformly mixed, thus corresponds to the lowest concentration of the regenerant species in the effluent from the Regenerant Displacement stage. Clearly, intercepting this effluent at an earlier stage, that is, a higher regenerant species concentration, would allow a greater volume of the effluent to be used in the preparation of the regenerant for the succeeding regeneration cycle.

In light of the preceding discussion, it would thus be appropriate to represent the regenerant species concentration profile in the model. As an illustration of this, a plug flow profile (Figure 6.4) is assumed for the regenerant species concentration in the effluent from the Regenerant Displacement stage and incorporated into the model. In considering this change to the optimisation model, it is noted that the residence time distribution is unlikely to conform to a plug flow profile practically; this model does however represent the best case scenario in terms of the reuse of regenerant-containing effluents.
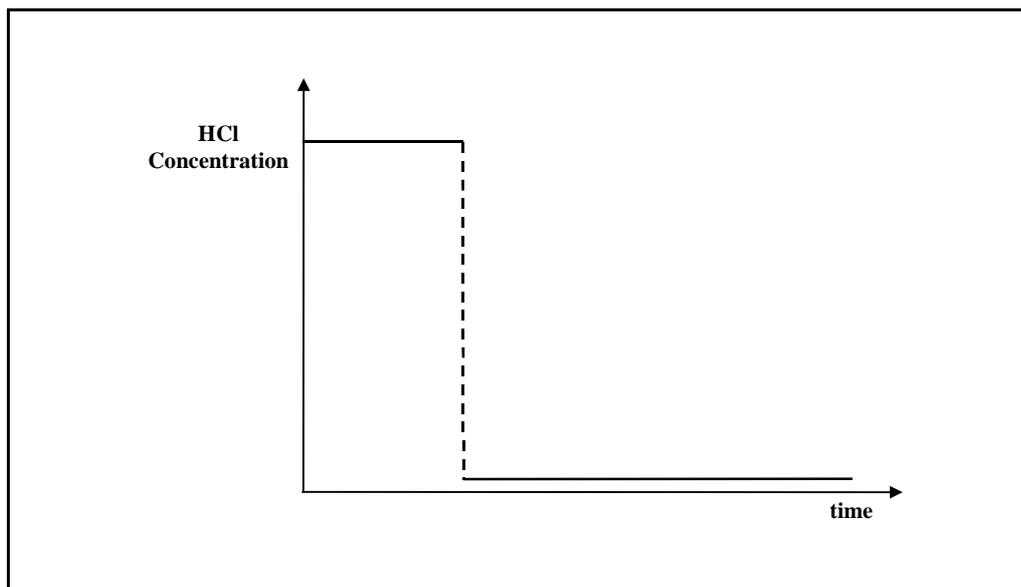
Figure 6.4. *Concentration profile for HCl in the effluent emerging during the Regenerant Displacement stage of the demineralisation plant regeneration (cation-exchange resin bed).*

Table 6.4 presents the results obtained from the optimisation of the demineralisation plant subsystem model which includes the effluent concentration profile for the regenerant species presented in Figure 6.4. The proposed network configuration is presented in Figure 6.5.

Table 6.4. *Comparison of the performance of the demineralisation plant in its existing configuration and the modified optimal configuration as projected over an annual period (360 days). The comparison is based on a fixed amount of demineralised water being available to the rest of the plant.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Demineralised Water Requirement by Rest of Plant	[t/y]	107 733	107 733	-
Duration of Normal Cycle of Operation	[h]	16	13.19	-
Regeneration Cycles	[cycles/y]	450	528	-
Umgeni Water	[t/y]	57 407	0	100
Umbogintwini River Water	[t/y]	57 407	110 270	-92
Total Water	[t/y]	114 814	110 270	4
Hydrochloric Acid (31% m/m HCl)	[t/y]	158	121	23
Caustic Soda (32% m/m NaOH)	[t/y]	176	134	23
Effluent	[t/y]	10 100	2 784	72
Total Cost*	[R/y]	540 667	364 161	33
Unit Cost of Demineralised Water*	[R/t]	4.71	3.16	33

* *These costs correspond to those for the year 2000.*

With the incorporation of the effluent concentration profile for the Regenerant Displacement stage in the demineralisation process module, further improvements in the utilisation of materials is shown to be possible. In particular, all of the effluent from the both the Regenerant Displacement stage and Fast Rinse stage is recovered. This results in a 72% reduction in the volume of effluent generated, relative to the existing configuration, with the unit cost associated with the demineralised water being reduced to R 3.16 per ton. It is of course noted that the assumed concentration profile represents an ideal situation and these results would be optimistic. A more realistic profile could nevertheless be easily incorporated.
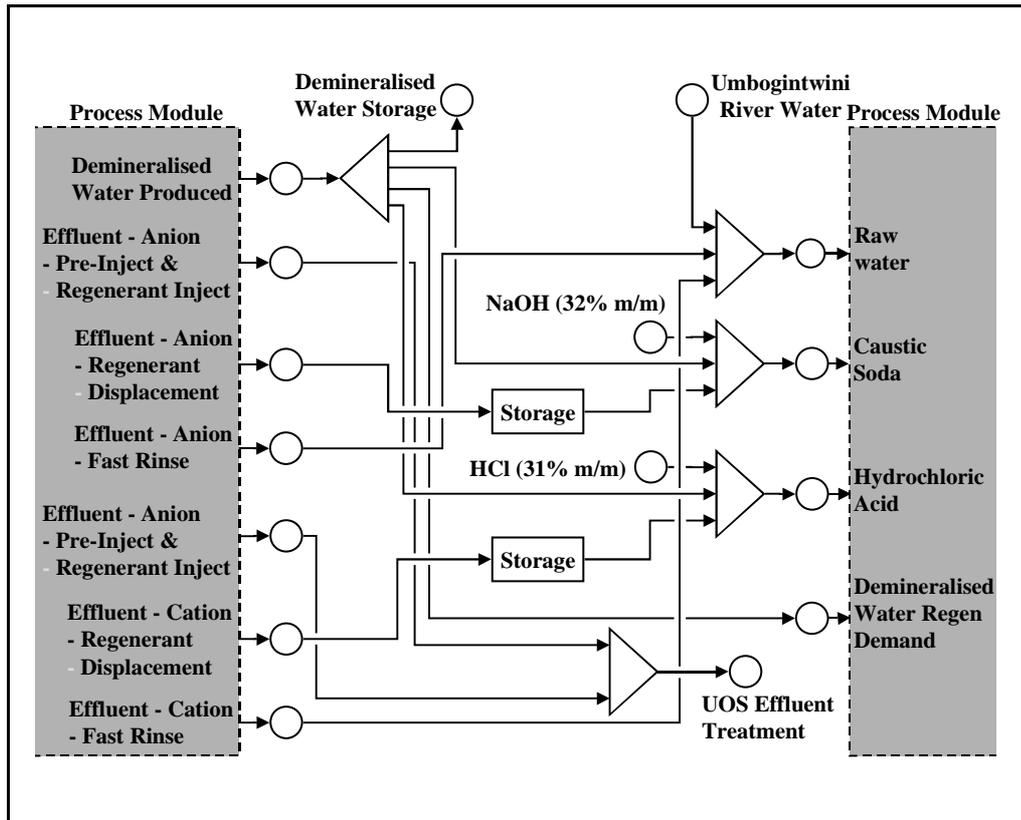
Figure 6.5. *Diagram showing the modified network configuration for the demineralisation plant subsystem. This configuration arises when the plug flow effluent concentration profile associated with the Regenerant Displacement stage of the regeneration sequence is incorporated in the optimisation model.*

In light of these considerations on the concentration profile of the reagent species in the effluent, it is appropriate to question the logical exclusion of the possibility of reusing effluent from the Pre-Inject & Regenerant Inject stage in the preparation of the regenerants for the succeeding regeneration cycle. There are however two residence time distribution considerations associated with this option. Firstly, there will be a residence time distribution profile associated with the progression of water hold-up in the resin bed at the start of the Regenerant Inject stage and secondly, there will be a residence time distribution profile associated with the elution of ions from the ion-exchange resin by the regenerants during the Regenerant Inject stage. In particular, there will be a point along the latter profile at which the concentration of removed ions in the effluent is low enough such that the effluent is of suitable quality for recovery. In determining this point at which regenerant recovery begins, suitable concentration profile data are required. These profiles may similarly be incorporated into the process module. While not intended to be an accurate representation, Figure 6.6 provides a visual illustration of these concepts.
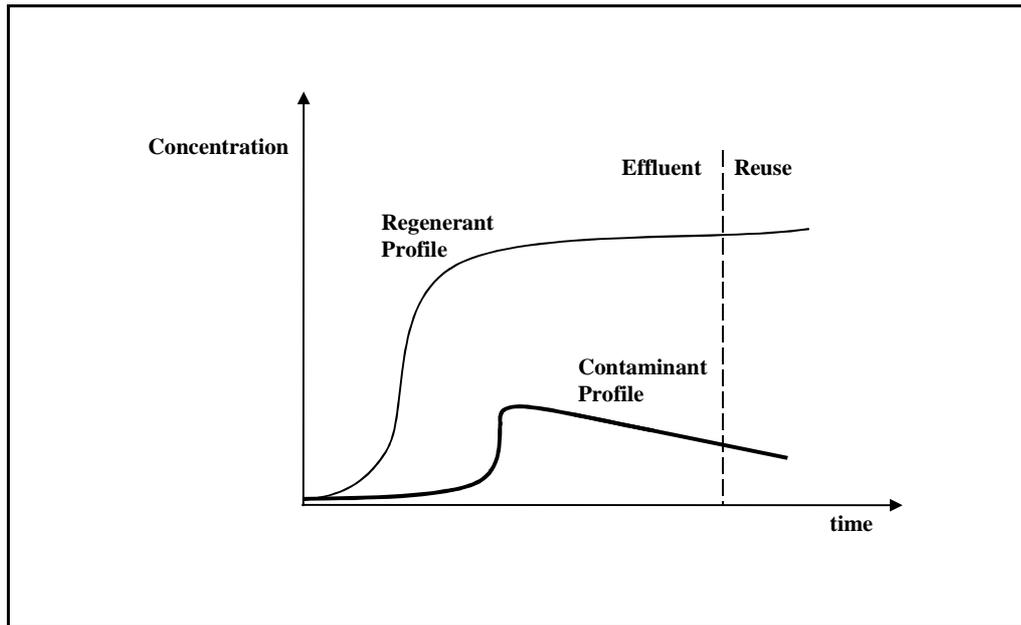
Figure 6.6. *Concentration profiles of the regenerant and contaminant species in the effluent emerging from the Pre-Inject & Regenerant Inject stage of the regeneration procedure. These profiles show a hypothetical point at which the reuse of regenerant-containing effluent may be possible.*

As a final comment on the demineralisation plant subsystem, the quality of the water sources available for treatment by demineralisation will be variable, and particularly seasonal. The use of one water source rather than the other is based on the ratio between cost and ionic load. Given the variability associated with the water quality, benefit may be derived from running the optimisation on a regular basis as seasons and material costs change. It is noted that for the problem at hand, it is only economically feasible to use the municipal supply of water when its cost decreases from R 3.26 per ton to R 2.64 per ton.

6.2.2 The Chemical Production Subsystem

The network configuration for the chemical production subsystem, as determined by optimisation, involves 74 connections between sources and sinks of the subsystem; some 39 of these connections are not present in the existing configuration. Given the complexity of this solution, it is not deemed feasible to represent the network configuration diagrammatically as was done for the demineralisation plant subsystem. The reuse matrix showing the mass flows of materials between the various sources and sinks associated with the subsystem is however presented in **Appendix D**. This section considers the results obtained from the optimisation of the chemical production subsystem in isolation from the other subsystems. **Section 6.2.2.1** considers the solution in a general sense and highlights some of the notable connections that are proposed. From this stage, the discussion branches into two areas. The first of these areas pertains to the global insight into the significance of the solution as derived from an analysis of the marginal values provided by the optimisation (**Section 6.2.2.2**). The second area involves a consideration of whether the proposed solution is practically realisable (**Section 6.2.2.3**).

6.2.2.1 Features of the Optimal Configuration for the Chemical Production Subsystem

Table 6.5 presents a comparison between the daily water and material consumption and effluent production figures associated with the existing and proposed network configurations for the chemical production subsystem. These figures include only those elements of the subsystem represented in the optimisation model. It is noted further that these figures pertain to the optimisation of the chemical production subsystem in isolation from all other subsystems. For this task, as has been noted previously, production levels and existing demands associated with the subsystem have been maintained at their existing levels, as has the unit cost associated with demineralised water. The following points are highlighted regarding the material consumption and effluent production figures for the proposed network configuration:

- The optimal network configuration shows a reduction of 58 % in the amount of water used and a reduction of 56 % in the amount of effluent produced by those elements of the subsystem included in the optimisation model.

- There are slight improvements in the consumption of raw salt, hydrochloric acid, caustic soda, sodium bisulphite, alpha-cellulose and chlorine gas. The proposed network configuration however uses more sodium carbonate, flocculant and steam.

- The salt load associated with the effluent has decreased slightly from the existing configuration but there is a slight increase in the NaOH mass-load.

- The optimal configuration shows a slight decrease in the regeneration frequency for the ion-exchange plant.

Some of the notable topological features of the proposed network configuration as observed from the material reuse matrix presented in **Appendix D** are as follows:

- Demineralised water is only used at the caustic soda dilution demand associated with the electrolyser process module; this was a process requirement. All other water demands are satisfied by water sources within the subsystem rather than external sources.

- The condensate from the chlorine cooler is routed to the sodium hypochlorite synthesis plant rather than through the dechlorinators.

Table 6.5. *Comparison of water and material requirements and effluent production associated with the existing network configuration and the optimal network configuration for the chemical production subsystem. This comparison only reflects those areas of the subsystem considered in the optimisation.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Demineralised Water	[t/d]	198.09	98.64	50
Umbogintwini River Water	[t/d]	34.62	0	100
Total Water	[t/d]	232.71	98.64	58
Raw Salt	[t/d]	142.96	142.71	0.17
Hydrochloric Acid (31% m/m HCl)	[t/d]	7.18	6.73	6.2
Caustic Soda (32% m/m NaOH)	[t/d]	67.21	66.82	0.6
Caustic Soda (38% m/m NaOH)	[t/d]	0	0	-
Caustic Soda (50% m/m NaOH)	[t/d]	0	0	-
Sodium Carbonate	[t/d]	1.056	1.061	-0.53
Sodium Bisulphite	[kg/d]	359.5	353.7	1.6
Flocculant	[kg/d]	7.77	8.03	-3.3
Alpha-Cellulose	[kg/d]	31.1	29.0	6.6
Chlorine	[t/d]	14.73	14.72	0.1
Steam	[t/d]	70.80	71.67	-1.2
Effluent	[t/d]	235.19	104.19	56
Solid Waste	[kg/d]	39.9	37.6	5.6
NaCl Load to Effluent	[t/d]	14.20	13.73	3.3
NaOH Load to Effluent	[kg/d]	39.9	84.0	-110
Duration of Normal Cycle of Operation of Cation-Exchanger	[h]	72	72.56	-
Annual Saving*	[R/y]		730 313	-

* *These costs correspond to those for the year 2000.*

- Effluent from the cation-exchange regeneration sequence is almost completely recovered. The effluents from the various stages of the regeneration sequence are used as follows:

  - Brine effluents from the Brine Displacement and Brine Replacement stages are routed to the brine inlet associated with the precipitation process module.

- A portion of the effluent from the Backwash stage is used to satisfy, in part, the water demand for the succeeding regeneration cycle; another portion is used in the preparation of the dilute caustic soda required for the succeeding regeneration cycle. The balance is sent to effluent.

- A portion of the effluent from the Acid Displacement stage is used in the preparation of the dilute hydrochloric acid required for the succeeding regeneration cycle. The balance is routed to the hydrochloric acid demand associated with the electrolyser process module. The effluent from the Acid Regeneration stage is similarly routed to the hydrochloric acid demand associated with the electrolyser process module.

- A portion of the effluent from the Caustic Regeneration stage is used in the preparation of the caustic soda required for the succeeding regeneration cycle. The balance is used to satisfy, in part, the caustic soda demands associated with the precipitation process module and the hydrogen chloride scrubber. Effluent from the Caustic Displacement stage is used in part to satisfy the caustic soda demand associated with the succeeding regeneration cycle with the balance being routed to the sodium hypochlorite synthesis process module.

- Brine from the primary filtration stage is used for the backwash of the primary filter rather than brine from the secondary filtration stage.

- The brine purge is located between the secondary dechlorination stage and the resaturator as in the present configuration.

- Of the three sources of concentrated caustic soda available to the subsystem, only the 32 % m/m NaOH source is used.

In terms of these topological features, the following points are noted:

- In terms of the use of water within the subsystem, it is noted that no Umbogintwini River water is used. Umbogintwini River water is used in the current network configuration to dilute the waste sodium hypochlorite entering the Hydecat destruction plant. This demand is however completely satisfied by water-reuse in the optimal configuration.

  Upon closer examination of the solution however, it is noted that the quality associated with these water sources is better than that of the Umbogintwini River water. The only reason that the optimisation favours the use of these water sources ahead of the Umbogintwini River water is that they are available

for use at no cost. Given the superior quality of these water sources, the possibility does exist that they may be used more effectively in the production of demineralised water, a possibility which is explored when the subsystems are integrated (**Section 6.3**).

- The routing of the condensate from the chlorine cooler to the sodium hypochlorite synthesis plant represents a more economical routing strategy for this source.

- The recovery of the hydrochloric acid effluent to the demand associated with the electrolyser process module indicates that the cost incentive for hydrochloric acid recovery outweighs the cost of removing the additional mass-loads of calcium and magnesium from the brine circuit.

- Analogous reuse strategies to those observed for the demineralisation plant subsystem are observed for the effluents associated with the regeneration of the cation-exchange procedure, that is, the reuse of effluent to satisfy, in part, the demands associated with the succeeding regeneration cycle. Similar arguments to those presented in the analysis of the demineralisation plant subsystem on the inclusion of concentration profiles in the model are appropriate.

- The use of brine from the primary filtration stage for backwashing purposes suggests that this option is more economical than the current practice of using brine from the secondary filtration stage.

- A choice of locations for the brine purge is included in the superstructure for the problem. The positioning of the brine purge at the same location as that of the current network verifies that this is the economically optimal position for the purge.

- The use of 32% m/m NaOH caustic soda is more economical than using the more concentrated sources. As it turns out, it is the ratio of cost to the NaOH concentration which is the significant parameter which determines the feasibility of using the source.

Having reviewed the topological features of the proposed network configuration, some analysis of the changes in the material consumption figures by the subsystem is appropriate. These changes are attributable to a number of factors; Table 6.6 presents a listing of these factors as pertaining to the various materials.

Table 6.6. *Listing of materials and factors contributing to the change in consumption of these materials in the proposed network configuration.*

Material	Contributing factors resulting in net change
Raw Salt	**Factors:** - Brine effluent from the cation-exchange regeneration is recovered. - Brine lost via the purge and brine sludge are slightly higher. **Result:** Net Decrease
Hydrochloric Acid (31% m/m HCl)	**Factors:** - HCl-containing effluent from cation-exchange regeneration is recovered. **Result:** Net Decrease
Caustic Soda (32% m/m NaOH)	**Factors:** - NaOH-containing effluent from cation-exchange regeneration is recovered. - Less caustic soda is used on secondary dechlorination due to decreased Cl_2 and HCl load in the brine from primary dechlorination. This is due to the rerouting of condensate from the chlorine cooler. - More caustic soda is used for precipitation due to an increased $MgCl_2$ load. This is caused by the recovery of HCl-containing effluent from the cation-exchange regeneration. **Result:** Net Decrease
Sodium Carbonate	**Factors:** - More sodium carbonate is used for precipitation due to an increased $CaCl_2$ load. This is caused by the recovery of HCl-containing effluent from the cation-exchange regeneration. **Result:** Net Increase
Sodium Bisulphite	**Factors:** - Less sodium bisulphite is used due to a decreased Cl_2 load in the brine from primary dechlorination. This is due to the rerouting of the condensate from chlorine cooler. **Result:** Net Decrease
Flocculant	**Factors:** - More flocculant is used due to an increased solids (precipitate) load on the clarifier. This is caused by the recovery of HCl-containing effluent from cation-exchange regeneration. **Result:** Net Increase
Alpha-Cellulose	**Factors:** - Less alpha-cellulose is used due to a reduced solids load on the secondary filter. This is caused by the use of brine from primary filtration rather than secondary filtration for the backwash of the primary filters. **Result:** Net Decrease
Chlorine	**Factors:** - Less chlorine is required for sodium hypochlorite synthesis due to the rerouting of condensate from chlorine cooler. **Result:** Net Decrease
Steam	**Factors:** - More steam is required due to an increased caustic soda throughput on caustic evaporation. This is due to the decrease in the internal use of caustic soda. **Result:** Net Increase

Table 6.7 presents a comparison of the consumption figures for the entire chemical production subsystem in its existing and proposed configurations. These figures include those elements of the chemical production subsystem not included in the optimisation.

Table 6.7. *Comparison of water and material requirements and effluent production associated with the existing network configuration and the optimal network configuration for the chemical production subsystem. This comparison reflects all areas of the chemical production subsystem, including those elements not considered in the optimisation.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Demineralised Water	[t/d]	289.74	190.30	34
Umbogintwini River Water	[t/d]	39.94	5.32	87
Total Water	[t/d]	329.68	195.62	41
Raw Salt	[t/d]	142.96	142.71	0.16
Hydrochloric Acid (31% m/m HCl)	[t/d]	7.62	7.17	5.8
Caustic Soda (32% m/m NaOH)	[t/d]	67.21	66.82	0.6
Caustic Soda (38% m/m NaOH)	[t/d]	0	0	-
Caustic Soda (50% m/m NaOH)	[t/d]	0	0	-
Sodium Carbonate	[t/d]	1.056	1.061	-0.53
Sodium Bisulphite	[kg/d]	359.5	354	1.6
Flocculant	[kg/d]	7.77	8.03	-3.3
Alpha-Cellulose	[kg/d]	31.1	29.0	6.6
Chlorine	[t/d]	32.78	32.77	0.05
Hydrogen	[kg/d]	723.3	723.3	-
Steam	[t/d]	70.80	71.67	-1.2
Effluent	[t/d]	240.71	109.70	54
Solid Waste	[kg/d]	39.9	37.6	5.6
NaCl Load to Effluent	[t/d]	14.2	13.7	3.3
NaOH Load to Effluent	[kg/d]	39.9	84.0	-110

Having explored the proposed network configuration in some detail, there are two distinct areas of consideration that emerge. The first of these areas involves the identification of process interventions which could be effected to the system such that further improvement in performance may be achieved. The second area sees attention being directed toward the practicalities of implementing the proposed reuse strategy. Included in this discussion is an assessment of the validity of the solution proposed by the optimisation. Each of these areas is considered in turn.

6.2.2.2 *Chemical Production Subsystem Solution Analysis*

In analysing the marginal values for the chemical production subsystem, it is assumed that the parameters related to the design and performance of the various process modules are representative of the actual design and performance of the operations involved. Any sensitivities reported by the optimisation must therefore correspond to the quantities and qualities of materials entering the subsystem. Figure 6.7 shows the non-zero species inlet concentration sensitivities for the chemical production subsystem. The constraints with which these marginal values are associated are part of the set of pinch constraints which limit the performance of the chemical production subsystem.
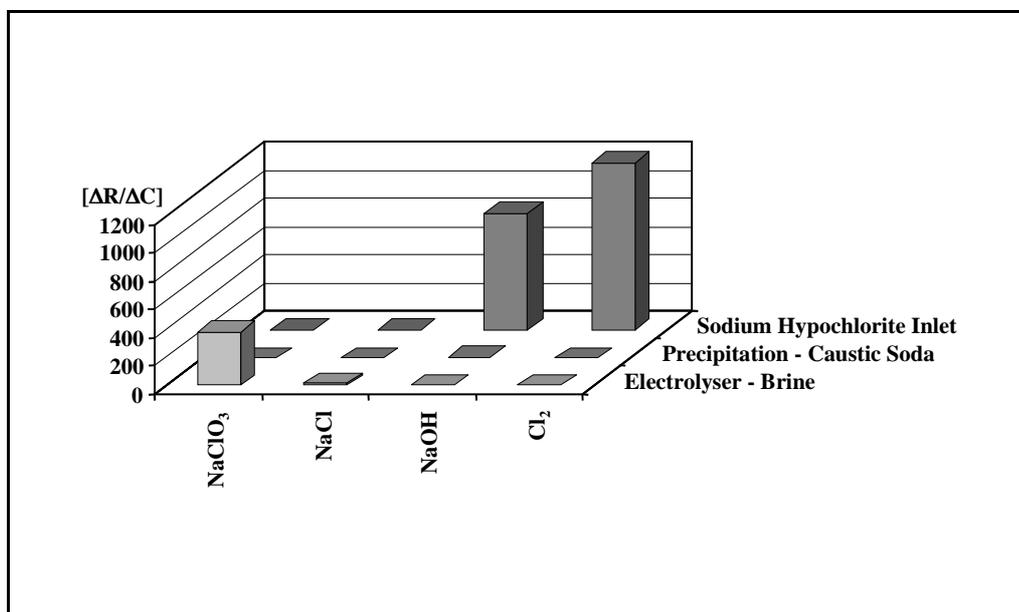
Figure 6.7. *Graphical representation of the non-zero marginal values associated with the concentration constraints of the different species at the inlets of process modules in the chemical production subsystem. Concentration is expressed in terms of mass fraction.*

From an analysis of Figure 6.7, the following points are made:

- The largest marginal values are reported for the concentration limits of Cl_2 and NaOH at the inlet of the sodium hypochlorite synthesis plant. Given that these are required at these concentrations for the production of sodium hypochlorite, no relaxation of these constraints is possible.

- Marginal values are reported for both NaCl and $NaClO_3$ at the inlet of the electrolyser. With the concentration constraint for NaCl being a process requirement, no relaxation of this constraint is possible. The concentration constraint related to $NaClO_3$ presents a more interesting case however.

Seemingly it is this constraint which prevents a further reduction in the objective variable. Thus, attention should be focussed on assessing whether this particular constraint can be relaxed. A careful analysis of the involvement of $NaClO_3$ in the brine circuit however reveals other options.

The $NaClO_3$ load arises in the brine circuit solely due to its generation in the electrolyser, that is, there are no other sources of $NaClO_3$ entering the circuit. Concentration levels in the brine circuit are regulated through the brine purge with a certain mass-load of the species also being removed from the circuit alongside the brine sludge. In the proposed network configuration, it is thus $NaClO_3$ that determines the purge flow from the brine circuit. It is through a decrease in this flow that an improvement in the objective variable arises. If the introduction of a treatment process which reduces the level of $NaClO_3$ in the circuit is excluded as a possibility, there are two routes to reducing the purge flow. The first involves an adjustment to the operating conditions in the electrolyser such that the level of $NaClO_3$ generated is reduced. The second route involves the relaxation of the species concentration limit at the inlet to the electrolyser such that a higher $NaClO_3$ load is circulated around the brine circuit. While these two options are noted, only the latter is explored.

According to the warranty on the electrolyser membranes, it is possible to relax the concentration limit on $NaClO_3$ by a small amount. When this is done and the chemical production subsystem optimised once more, the purge flow is reduced, but only until the concentration limit on Na_2SO_4 is reached. Further relaxation of the $NaClO_3$ concentration constraint does not reduce the purge flow further and thus has no effect on the value of the objective variable and the material consumption figures. In this situation it is the Na_2SO_4 concentration constraint at the inlet of the electrolyser which becomes part of the set of pinch constraints.

A similar analysis of how the Na_2SO_4 load arises in the circuit should be conducted. Relaxation of this concentration constraint is not possible within the limitations specified by the warranty on the electrolyser membranes. Other opportunities for reducing the load in the circuit would thus need to be explored. Having demonstrated the approach required in analysing the solution provided by the optimisation, further exploration of this area is not considered. Table 6.8 presents the consumption figures pertaining to the modified problem.

- A small marginal value is reported for the concentration limit of NaOH at the caustic soda inlet to the precipitation process module. Due to the magnitude of this sensitivity, it is not explored.

It is noted that the analysis of results presented here does not represent an exhaustive examination of the insight they can provide. Nevertheless, the approach is considered to be have been demonstrated adequately.

Table 6.8. *Comparison of water and material requirements and effluent production associated with the existing network configuration and the modified optimal network configuration for the chemical production subsystem. The comparison only reflects those areas of the subsystem considered in the optimisation.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Demineralised Water	[t/d]	198.09	98.64	50
Umbogintwini River Water	[t/d]	34.62	0	100
Total Water	[t/d]	232.71	98.64	58
Raw Salt	[t/d]	142.96	142.27	0.48
Hydrochloric Acid (31% m/m HCl)	[t/d]	7.18	6.73	6.2
Caustic Soda (32% m/m NaOH)	[t/d]	67.21	66.82	0.6
Caustic Soda (38% m/m NaOH)	[t/d]	0	0	-
Caustic Soda (50% m/m NaOH)	[t/d]	0	0	-
Sodium Carbonate	[t/d]	1.056	1.061	-0.50
Sodium Bisulphite	[kg/d]	359.5	353.7	1.6
Flocculant	[kg/d]	7.77	7.97	-2.5
Alpha-Cellulose	[kg/d]	31.08	28.98	6.7
Chlorine	[t/d]	14.73	14.72	0.1
Steam	[t/d]	70.80	71.67	-1.2
Effluent	[t/d]	235.19	103.75	56
Solid Waste	[kg/d]	39.86	37.17	6.7
NaCl Load to Effluent	[t/d]	14.2	13.3	6.3
NaOH Load to Effluent	[kg/d]	39.9	83.3	-109
Duration of Normal Cycle of Operation of Cation-Exchanger	[h]	72	72.49	-
Annual Saving*	[R/y]	-	771 571	-

* *These costs correspond to those for the year 2000.*

6.2.2.3 Implementation and Validity Considerations for the Chemical Production Subsystem

Having explored the proposed network configuration in some detail and examined the analytical implications of the results, attention shifts to assessing the validity of the initial reuse strategy identified by the optimisation. This being established, attention shifts to the implementation of this reuse strategy.

From a mathematical perspective, the initial reuse strategy provided by the optimisation is considered valid due to:

- The concentration constraints associated with the various demands are all satisfied;

- The required production rates of chlorine, hydrochloric acid and sodium hypochlorite are observed; and

- The proposed configuration is similar to the current configuration in terms of the transformation of raw materials to products.

In **Chapter 5**, it was noted that there is an implicit assumption in the formulation of the process modules that the performance of the operations they represent is independent of the inlet species concentrations to the operations. The only way this assumption can be verified is through simulation or plant trials. As a comment however, it is noted that the changes in the concentrations of species to the various processes in the optimal configuration is not largely different from those of the current configuration. These models should therefore be reasonably representative of the performance of the actual operations in the optimal configuration. However, again, this can only be verified by simulation or plant trials.

While validity from these perspectives is an important issue, there are other issues involved in implementing the proposed solution. As such, one criticism of the proposed network configuration is that it divides streams into several smaller branches. Such configurations are difficult to control and costly to implement. The obvious way around this problem involves the inclusion of further mixed integer constraints of the form:

$$\sum_{j} Z_{i,j} \leq N_{i,max} \qquad\qquad 6.5$$

$$\sum_{i} Z_{i,j} \leq N_{j,max} \qquad\qquad 6.6$$

where $N_{i,max}$ is the maximum number of branches that secondary source i may be divided into and $N_{j,max}$ is the maximum number of branches which may combine to feed sink j. However, with the complexity of the model involved, convergence problems were encountered when the model was solved as an MINLP. The solution of the model as an RMINLP may provide some improvement in the number of connections, but with the mixed integer variables being treated as continuous, there is no guarantee that they will be strictly adhered to. Another option is to make appropriate changes to the connectivity matrix such that the number of connections is reduced, though this may be tedious.

Given these problems, another strategy for implementation is presented. As noted already, there is a large number of connections (39) present in the network configuration proposed by the optimisation which are not present in the existing configuration. As such, there will be a

different cost incentive associated with each of these proposed source-sink matches. In moving towards implementation, it is necessary to identify and prioritise which of these connections are the most promising such that they may be investigated further. Some criterion is however required such that priority may be assigned to the various matches. The proposed prioritising method involves an evaluation of the proposed connections on the basis of the cost of replacing the match with external sources and the cost associated with the disposal of the original source. Using the brine effluent from the cation-exchange regeneration sequence as an example, its ranking is based on the sum of two costs. The first cost involves the cost of raw salt and demineralised water required to produce a source equivalent to the effluent. The second cost reflects the expense involved in routing the brine effluent to the effluent treatment facility. Table 6.9 shows the alternate connections ranked in order of decreasing value. These connections are further represented as a proportion of the sum of the ranking costs across all connections. The cumulative percentage is also shown. It is noted that only the top third of the matches are shown in this table.

Table 6.9. *Listing of the more economically attractive source-sink matches proposed by the optimisation in order of descending ranking cost.*

Match	Flow [t/d]	Proportion [%]	Cumulative Percentage [%]
Water from collection drain to precipitation	21.908	12.15	12.15
Chlorine condensate to sodium hypochlorite synthesis	18.925	9.23	21.38
Effluent from Acid Regeneration to hydrochloric acid demand on electrolyser process module	2.089	6.62	28.00
Effluent from Brine Displacement to precipitation	5.478	6.44	34.44
Effluent from Acid Displacement to hydrochloric acid demand on electrolyser process module	3.572	6.43	40.87
H_2 cooler condensate to precipitation	11.081	6.14	47.01
H_2 cooler condensate to cation-exchange regeneration - water demand	8.879	4.92	51.93
Effluent from Caustic Displacement to sodium hypochlorite synthesis	5.237	4.51	56.44
Water from collection drain to cation-exchange regeneration - water demand	7.738	4.29	60.73
Water from collection drain to flocculant dilution	6.913	3.83	64.57
Effluent from Acid Displacement to cation-exchange regeneration - hydrochloric acid demand	1.73	3.11	67.68

cont.

Table 6.9. *cont.*

Match	Flow [t/d]	Proportion [%]	Cumulative Percentage [%]
Effluent from Caustic Displacement to cation-exchange regeneration - caustic soda demand	2.197	2.89	70.57
Effluent from Brine Replacement to precipitation	1.764	2.89	73.46

The following points are noted regarding the listing of ranking costs presented in Table 6.9:

- Notably, the flowrate associated with a proposed match is not an indication of its economic attractiveness as an option. In particular, the third most economically attractive option has the third smallest flowrate in Table 6.9.

- Significantly, some 70 % of the potential savings are accrued through less than a third of the proposed matches.

In light of these considerations, it is proposed that the matches highlighted in Table 6.9 form the basis of the reuse strategy. While this will not provide the full integration benefit, it is probably representative of what is achievable practically. If these matches are analysed, the areas of reuse to target are roughly as follows (Table 6.10):

Table 6.10. *Listing of the more economically attractive reuse schemes as identified by an analysis of the proposed source-sink matches.*

Match	Percentage of Sum of Rankings
Reuse of effluent from cation-exchange regeneration	36
Reuse of effluent from collection drain	22
H_2 Cooler condensate reuse	11

One further option which may be investigated is the recovery of the effluent from the pump seals. This water is considered to be of high quality and although there are several sources of this water, collectively, these sources account for approximately 20 % of the total ranking cost.

6.2.3 The Cooling Circuit Subsystem

Having demonstrated the approach to analysing the solution provided by the optimisation in the other two subsystems, the results from the optimisation of the cooling circuit subsystem are considered only briefly. Table 6.11 presents a comparison of the water consumption and effluent production figures for the existing network configuration and the proposed network configuration. The proposed network configuration is shown in Figure 6.8. The reuse matrix showing the distribution of material between the various sources and sinks associated with the subsystem is presented in **Appendix D.**

Table 6.11. *Comparison of the water requirement and effluent production associated with the existing network configuration and the optimal network configuration for the cooling circuit subsystem.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Umbogintwini River Water	[t/d]	846.62	828.16	2
Effluent	[t/d]	128.12	109.66	14
Annual Saving	[R/y]	-	67 188	-

* *These costs correspond to those for the year 2000.*
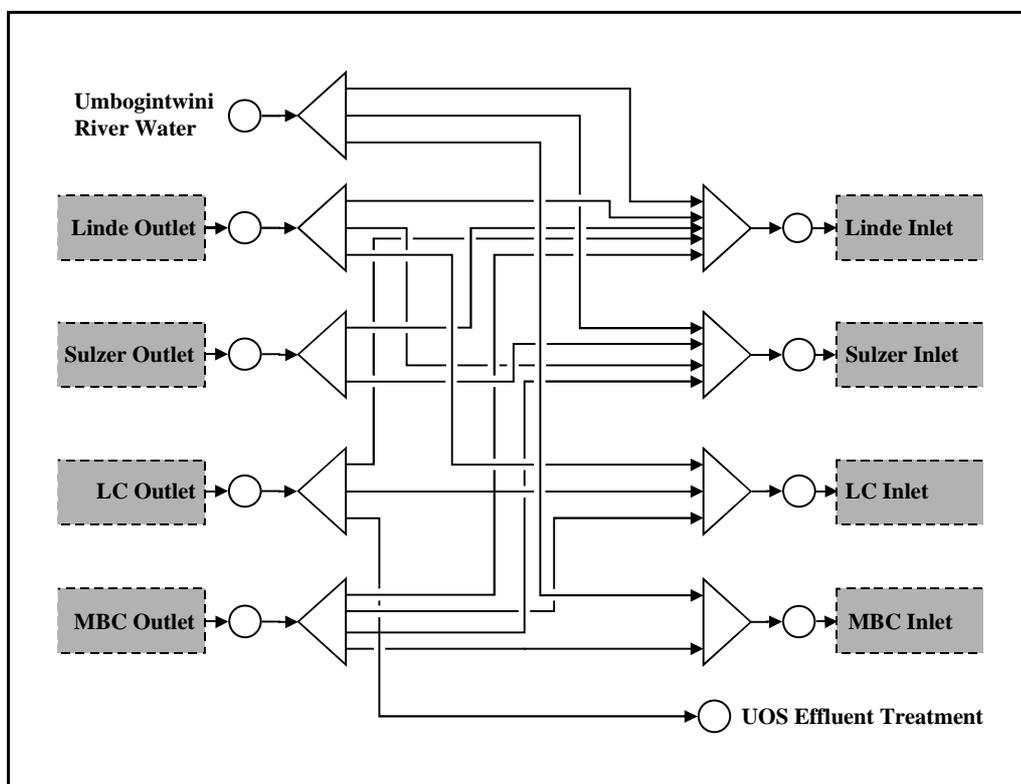
Figure 6.8. *Diagram showing the optimal network configuration for the cooling circuit subsystem.*

In terms of the figures presented in Table 6.11 and the proposed network configuration shown in Figure 6.8, the following points are made:

- The savings in water consumption and effluent production are not as significant as those for the other subsystems.

- In terms of the proposed network configuration, only the Linde, Sulzer and MBC cooling circuits use Umbogintwini River water as make-up. The make-up demands associated with the LC cooling circuit is satisfied by using the blowdown volumes from the different cooling circuits. The LC cooling circuit is the only circuit which sends a volume of water to the effluent treatment facility.

It should be noted that constraints specifying blowdown volumes are not included in the models for the process modules. These are determined during the course of the optimisation and are subject to the inlet concentration limits of the cooling towers (which are maintained at their existing concentrations initially). This produces a solution which routes large quantities of water from one cooling tower to another, an option which will be costly to implement from a pumping point of view. In practice, there are numerous designs which will achieve the targeted flowrate for the system and a less expensive option, in terms of pumping costs, is sought. For this reason, additional constraints are added to the optimisation model so that the direct recycle of water to the various cooling towers is maximised. These constraints are however adjusted such that there is no increase in the objective variable for the problem. For this problem this is consistent with there being no change in the amount of water used and effluent produced by the system. The network configuration presented in Figure 6.8 corresponds to this modified problem. The comment is made that this design is somewhat complex; a simpler design configuration was however not explored.

An analysis of the marginal values provided by the optimisation shows that it is the concentration constraint associated with Na_2CO_3 at the inlet of the LC cooling tower that prevents a further improvement in the objective variable. The analysis should thus proceed to an investigation of the validity of this constraint. While this analysis is not considered further, the point is made that there is a reasonable amount of uncertainty inherent in the formulation of the model such that this should be the first area considered in this analysis. Notably, the aquatic speciation package MINTEQA2 (Allison et al., 1991) was used in determining how much carbonate would be present in the water in equilibrium with the atmosphere.

A further comment regarding the integration of the different cooling circuits is that an analysis of the energy-side of the problem would be needed before any implementation is considered.

6.3 SUBSYSTEM INTEGRATION

Having considered the optimisation of the three individual subsystems in isolation from each other, attention now shifts to the integration of these subsystems. Apart from exploring opportunities for water-reuse from one subsystem to another, the integration of the subsystems quantifies the performance of the subsystems as an integrated unit. In addition, a more realistic reflection of the potential savings accruable from the proposed reuse strategy is provided. Before the strategy for integrating the subsystems is described, it is necessary to consider some of the effects arising from the optimisation of the individual subsystems.

The first of these effects relates to the decrease in demand for demineralised water by the chemical production subsystem. In line with this decrease, the demineralisation plant could either decrease its rate of production of demineralised water or could continue at its present rate of production with the spare demineralised water being exported from the complex or used elsewhere. If the export of demineralised water is excluded as a possibility, then the water might be used in the cooling circuit subsystem, but only if economically feasible. If it is not economically feasible, then the rate of production of demineralised water should decrease.

It has been noted previously that there are a number of good quality water sources present within the chemical production subsystem which might be more effectively used in the demineralisation plant subsystem. In the network configuration proposed by the optimisation of the chemical production subsystem in isolation from the other subsystems, these water sources are routed to the Hydecat destruction plant. It is however feasible to use Umbogintwini River water for this purpose instead.

In verifying this scenario, a fictitious sink was added to the model for the chemical production subsystem. Given that the quality associated with the water sources of interest is superior to that of Umbogintwini River water, a recovery cost factor, equivalent to the saving in treatment costs which would be achieved by routing these water sources to the demineralisation plant, was attached to this sink. When the model is optimised once more, Umbogintwini River water is used at the Hydecat destruction plant instead of these good quality water sources, which are now routed to the fictitious sink in the new configuration. It is this water which is available for use in the demineralisation plant subsystem.

One complication in integrating the various subsystems comes with the model for the demineralisation plant subsystem being based on the production of a particular quantity of water. The model for the chemical production subsystem is however based on daily production and is thus rate based. In integrating these two subsystems, the water available to the demineralisation plant from the chemical production subsystem must be converted to a quantity of water supplied per cycle rather than a continuous flowrate to the demineralisation plant. This quantity of water is equivalent to the product of the total cycle time for the demineralisation plant, that is, the time for one complete normal cycle of operation and one

regeneration cycle, and the rate of supply of this water from the chemical production subsystem.

The use of the good quality water from the chemical production subsystem in the production of demineralised water has the effect of decreasing the frequency of regeneration. With the demineralisation plant model being based on the production of a fixed quantity of water, this is equivalent to an increase in the proportion of the total feed water to the demineralisation plant supplied by the chemical production subsystem. With this water being available to the demineralisation plant at no cost (excluding pumping costs), the unit cost of the demineralised water decreases.

As noted previously, spare demineralised water may be used in the cooling circuit subsystem, if economically feasible. At present it is the higher cost associated with the demineralised water which prevents any from being used in the cooling circuit subsystem. In terms of the decrease in the unit cost of demineralised water, a point must be reached where it becomes economically feasible to use any spare demineralised water in the cooling circuit subsystem. In terms of integrating the subsystems, it is necessary to identify this point. In doing this, the availability limit on demineralised water was removed from the model for the cooling circuit subsystem. The cost factor associated with the use of demineralised water was reduced until such point where demineralised water was used in preference to the Umbogintwini River water presently used. While the exact point was not identified, it was found that for a demineralised water cost factor of R 2.693 per ton, only demineralised water was used by the subsystem while for a demineralised water cost factor of R 2.695 per ton, only Umbogintwini River water was used[1]. From this analysis, it may be concluded that it is feasible to use demineralised water in the cooling circuit subsystem if the unit cost of demineralised water decreases below R 2.695 per ton.

The use of demineralised water in the cooling circuit subsystem has the effect of increasing the overall demand for demineralised water. This results in an increase in the regeneration frequency of the demineralisation plant. With this increase in regeneration frequency, the proportion of the total feed water to the demineralisation plant supplied by the chemical production subsystem decreases and the unit cost of the demineralised water increases once again. As such, the use of demineralised water is only economically feasible as long as the unit cost for demineralised water remains below R2.695 per ton. It is thus possible to use any additional demineralised water in the cooling circuit but only to the extent that the unit cost does not rise above the threshold value. This value is thus a significant point in the integration strategy since it marks the change in the pattern of use of the demineralised water.

One further effect of the changing regeneration frequency is that it changes the amount of caustic soda required for the regeneration of the demineralisation plant. This amount must be supplied from the chemical production subsystem. A decrease in the regeneration frequency results in a decrease in the demand for caustic soda by the demineralisation plant. This in turn

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[1] *Within the unit cost range R 2.693 per ton to R 2.695 per ton, a combination of Umbogintwini River water and demineralised water is used, with the proportion of demineralised water increasing as the unit cost of demineralised water decreases.*

results in an increased throughput of caustic soda to the caustic evaporators. More steam is required to effect the evaporation and more condensate is produced from the evaporation process. The increase in the amount of condensate in turn will affect the amount of good quality water available for export to the demineralisation plant and thus brings further change in the regeneration frequency of the demineralisation plant.

In light of these considerations, an iterative procedure is required for the integration of the subsystems. This strategy is outlined as follows:

1   Initially, the assumption is made that there is no export of water from the chemical production subsystem to the demineralisation plant subsystem. In addition, it is assumed that the caustic soda demand from the demineralisation plant is the same as that of the existing network configuration. The unit cost of demineralised water is similarly assumed to be the same as that associated with the existing network configuration.

2   From the optimisation of the demineralisation plant subsystem, the quantity of water available to the rest of the plant, the amount of caustic soda required for regeneration in producing this quantity of water and the unit cost of demineralised water are recorded.

3   From the optimisation of the chemical production subsystem, the daily quantity of water available for export from the chemical production subsystem and the demand for demineralised water by those elements of the subsystem included in the optimisation model are recorded. The total daily demand for demineralised water by the chemical production subsystem is determined by incorporating the demand associated with those elements not included in the optimisation model.

4   Based on the chemical production subsystem's annual demand for demineralised water, the number of regeneration cycles per annum and the total cycle time for the demineralisation plant are calculated. As noted previously, the model for the demineralisation plant subsystem is based on the production of a particular quantity of demineralised water. Based on the calculated regeneration frequency, the time required for the demineralisation plant to produce this particular quantity of water is calculated. The amount of water available for export to the demineralisation plant subsystem from the chemical production subsystem during this period is then determined.

    The demineralisation plant subsystem model is updated to reflect this amount of water available from the chemical production subsystem and the model is optimised once more. As previously, the amount of caustic soda required for regeneration, the amount of demineralised water available to the rest of the plant and the unit cost of demineralised water are recorded.

5   Based on the results obtained from the optimisation of the demineralisation plant subsystem model, the daily demand for caustic soda is determined. The model for the chemical production subsystem is modified to reflect the updated unit cost of demineralised water and the updated caustic soda demand as derived from Step 4. From the optimisation of the chemical production subsystem, the daily quantity of water available for export and the daily demineralised water demand are recorded.

6   If the criteria for convergence is satisfied, the procedure stops at this point. If this criteria is not satisfied, Step 4 is repeated.

Within this strategy, it was noted that if the unit cost of demineralised water falls below the threshold value of R 2.695, the use of spare demineralised water in the cooling circuit must be included in the strategy. As it turned out, the unit cost for demineralised water remained above this threshold value and this element of the integration strategy was therefore not developed.

Table 6.12 presents a comparison between the annual material consumption and effluent production figures for various subsystems of the chlor-alkali complex in their existing configurations and those configurations proposed by the optimisation. These figures reflect the behaviour of the subsystems in combination with each other. The figures associated with the existing network configuration have been adjusted to reflect the performance of the various subsystems on an integrated basis. Table 6.13 combines the figures from Table 6.12 and presents a comparison between the two network configurations of the chlor-alkali complex in terms of the total consumption of materials and production of effluent.

Table 6.12. *Comparison of materials used and waste generated by the chlor-alkali complex in its existing network configuration and the optimal network configuration. These figures reflect the performance of the different subsystems in combination with each other.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Demineralisation Plant Subsystem				
Umbogintwini River Water	[t/y]	55 582	58 967	-6
Umgeni Water	[t/y]	55 582	0	100
Total Water	[t/y]	111 164	58 967	47
Demineralised Water Produced	[t/y]	111 144	71 679	36
Caustic Soda (32% m/m NaOH)	[t/y]	170	94	44
Hydrochloric Acid (31% m/m HCl)	[t/y]	153	85	44

cont.

Table 6.12. *cont.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Demineralisation Plant Subsystem				
Effluent	[t/y]	9 779	3 361	66
NaCl Load in Effluent	[t/y]	85	47	45
NaOH Load in Effluent	[t/y]	0.96	0.49	49
Annual Saving* (AS1)	[R/y]	-	294 615	-
Unit Cost of Demineralised Water	[R/t]	4.71	3.19	32
Number of Regeneration Cycles	[/y]	436	282	35
Duration of Normal Cycle of Operation	[h]	16.6	27.4	-
Chemical Production Subsystem				
Demineralised Water	[t/y]	104 308	68 507	34
Umbogintwini River Water	[t/y]	14 378	14 378	0
Total Water	[t/y]	118 686	82 885	30
Raw Salt	[t/y]	51 464	51 377	0.17
Sodium Carbonate	[t/y]	380	382.1	-0.54
Sodium Bisulphite	[t/y]	129.4	127.3	1.6
Caustic Soda (32% m/m NaOH)	[t/y]	24 196	23 881	1.3
Hydrochloric Acid (31% m/m HCl)	[t/y]	2 584	2 424	6.2
Chlorine	[t/y]	11 802	11 797	0.05
Hydrogen	[t/y]	260.4	260.4	0
Steam	[t/y]	25 487	25 828	-1.3
Flocculant	[kg/y]	2 797	2 890	-3.3
Alpha-Cellulose	[kg/y]	11 188	10 444	6.6
Effluent	[t/y]	86 655	39 287	55
NaCl Load in Effluent	[t/y]	5 047	4 945	2
NaOH Load in Effluent	[t/y]	14.36	30.22	-110
Solid Waste	[kg/y]	14 349	13 545	6
Annual Saving* (AS2)	[R/y]	-	584 844	-

cont.

Table 6.12. *cont.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Cooling Circuit Subsystem				
Umbogintwini River Water	[t/y]	304 782	298 136	2
Effluent	[t/y]	46 124	39 478	14
NaCl Load in Effluent	[t/y]	21.2	20.7	2
Annual Saving* (AS3)	[R/y]	-	66 268	-
Total Annual Saving* (AS1 + AS2 + AS3)	[R/y]	-	945 727	-

* *These costs correspond to those for the year 2000.*

Table 6.13. *Comparison of the total consumption of materials and waste generated across all subsystems of the chlor-alkali complex in its existing network configuration and the optimal network configuration.*

	Unit	Existing Configuration	Optimal Configuration	Percentage Improvement [%]
Umbogintwini River Water	[t/y]	374 743	371 481	0.9
Umgeni Water	[t/y]	55 582	0	100
Total Water	[t/y]	430 325	371 481	14
Demineralised Water	[t/y]	104 308	68 507	34
Caustic Soda (32% m/m NaOH)	[t/y]	24 366	23 975	1.6
Hydrochloric Acid (31% m/m HCl)	[t/y]	2 737	2 509	8.3
Raw Salt	[t/y]	51 464	51 377	0.17
Sodium Carbonate	[t/y]	380.0	382.1	-0.53
Sodium Bisulphite	[t/y]	129.4	127.3	1.6
Chlorine	[t/y]	11 802	11 797	0.05
Hydrogen	[t/y]	260.4	260.4	0
Steam	[t/y]	25 487	25 828	-1.2
Flocculant	[kg/y]	2 797	2 890	-3.3
Alpha-Cellulose	[kg/y]	11 188	10 444	6.6
Effluent	[t/y]	142 557	82 126	42
NaCl Load in Effluent	[t/y]	5 153	5 013	2.7
NaOH Load in Effluent	[t/y]	15.3	30.7	-100
Solid Waste	[kg/y]	14 349	13 545	5.6
Annual Saving*	[R/y]	-	945 727	-

* *These costs correspond to those for the year 2000.*

While similar trends are observed for the various subsystems to when they were considered in isolation from each other, the following points are noted regarding the results:

- The demineralisation plant shows a significant improvement in its performance with the decrease in the demand for demineralised water by the rest of the complex. Alongside this decrease, the frequency of regeneration decreases such that the normal cycle of operation is now 27.4 h instead of 16.6 h in the existing configuration. The unit cost associated with the demineralised water decreases from R 4.710 to R 3.193 which is above the threshold value for use in the cooling circuit subsystem.

  From Table 6.12 it appears that more water is produced by the demineralisation plant than is fed to it. The difference is however supplied by the sources from the chemical production subsystem.

- In terms of the chemical production subsystem, it is noted that there is no cost associated with the use of demineralised water. This cost is already represented in the economics for the demineralisation plant. A decrease in the amount of caustic soda required by the subsystem is observed compared to the demand associated with the subsystem when it is optimised in isolation from the other subsystems. This is due to an allowance being made in this model for the demand associated with the demineralisation plant subsystem. With the integration of the subsystems, this quantity is accounted for in the economics of the demineralisation plant subsystem.

- With the unit cost associated with the demineralised water remaining above the threshold value, the cooling circuit subsystem is unaffected by the integration of the subsystems.

- In total, the potential economic savings associated with the proposed network configuration amount to R 945 727 per annum based on costs from the year 2000. This solution achieves a 14 % reduction in the amount of water used by the complex and a 42 % reduction in the amount of effluent generated.

Figure 6.9 presents a schematic diagram showing the interactions between the various subsystems as they exist in the proposed optimal configuration. The demineralisation plant subsystem now treats raw water and regenerates effluent from the chemical production subsystem to a standard acceptable for use in the complex. This network configuration has the advantage that most of the retrofit work involves routing the effluent streams to the demineralisation plant. Once there, the piping is already in place to distribute the demineralised water to the appropriate demands. It is further noted that while the assumption was made that these effluent sources are of a quality similar to that of demineralised water, in reality there may be a slight level of contamination present in these sources. The use of the demineralisation plant subsystem in regenerating these sources thus ensures that the quality

requirements of the complex are met. The reuse matrix showing the distribution of material between the sources and sinks of the integrated subsystems is presented in **Appendix D**.
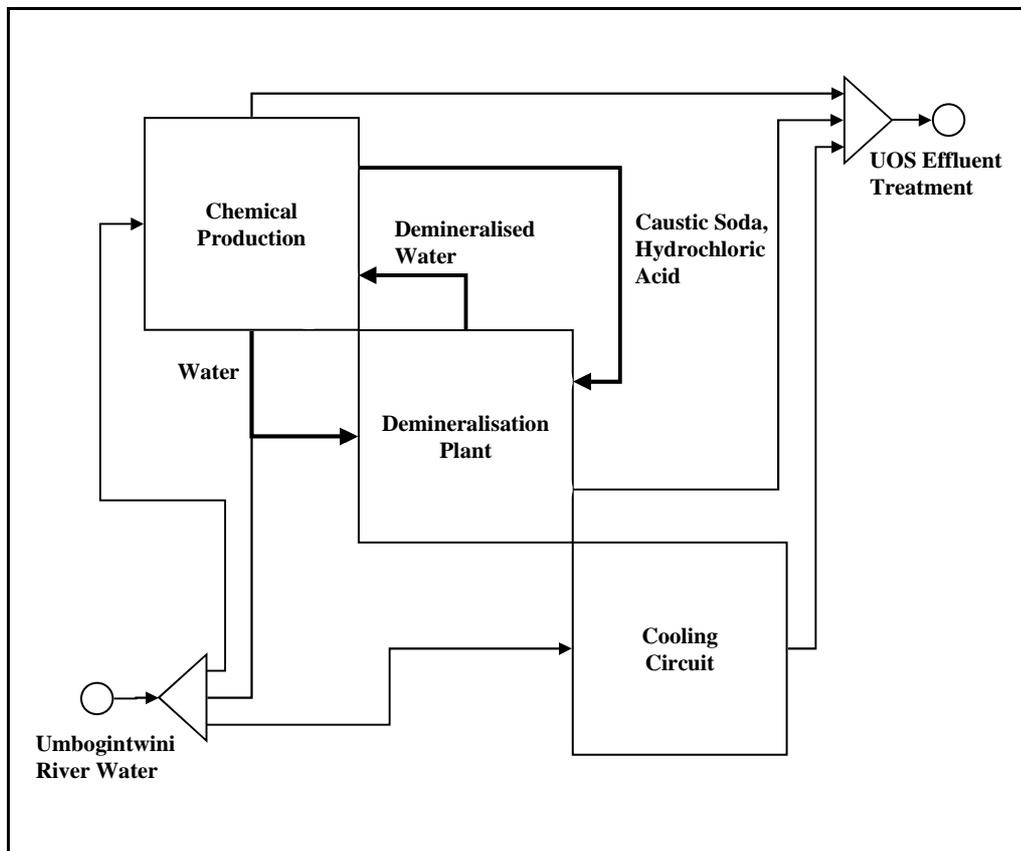
Figure 6.9. *Schematic diagram showing the distribution of water and collection of effluent from the subsystems of the chlor-alkali complex in its proposed optimal configuration. Interactions between the various subsystems as they exist in this configuration are also shown.*

6.4 PLACING THIS STUDY IN CONTEXT

Having considered the application of Combined Water and Materials Pinch Analysis to the chlor-alkali complex, it is appropriate to consider the results provided by this study in comparison to those achieved by the other studies. With several changes to the system having taken place since the initial study by Gardner (1999) it is appropriate only to consider the comparison in terms of the percentage savings achieved. Table 6.14 presents a comparison of the potential savings reported by Gardner, those reported for the Water Pinch Analysis study in **Appendix B** and the results from the Combined Water and Materials Pinch Analysis study.

Table 6.14. *Comparison of the percentage savings achieved by the three studies conducted at the chlor-alkali complex. These studies are the initial study by Gardner (1999), the Water Pinch Analysis study and the Combined Water and Materials Pinch Analysis study.*

	Initial Study [%]	Water Pinch Analysis [%]	Combined Water and Materials Pinch Analysis [%]
Umbogintwini River Water	N/A	7	0.9
Umgeni Water	N/A	42	100
Total Water	72	11	14
Demineralised Water	N/A	34	34
Caustic Soda (32% m/m NaOH)	2.9	0.2	1.6
Hydrochloric Acid (31% m/m HCl)	4.2	1.9	8.3
Raw Salt	N/A	0	0.17
Sodium Carbonate	N/A	0	-0.53
Sodium Bisulphite	N/A	0	1.6
Chlorine	N/A	0	0.05
Hydrogen	N/A	0	0
Steam	N/A	0	-1.2
Flocculant	N/A	0	-3.3
Alpha-Cellulose	N/A	0	6.6
Effluent	45	32	42
Solid Waste	N/A	0	5.6
Annual Saving* [R/y]	N/A	542 881	945 727

* These costs correspond to those for the year 2000.

In terms of these results Gardner reports water abstraction and effluent production savings in excess of those predicted by either the Water Pinch Analysis or Combined Water and Materials Pinch Analysis studies. The system considered by Gardner however included processes which were not present in the system considered by the other studies. In addition, Gardner did not include the cooling circuit in his analysis. As observed previously, the cooling circuit subsystem is the greatest user of water and producer of effluent out of the three subsystems. Given these considerations, it is difficult to draw comparisons between the initial study and those which followed and this comparison is not explored further.

The comparison between the Water Pinch Analysis study and the Combined Water and Materials Pinch Analysis study is however justified. The Water Pinch Analysis study was able to realise some 57% of the total saving achieved by Combined Water and Materials Pinch Analysis. In terms of water abstraction and effluent generation, relatively small changes are observed between these two studies with the Combined Water and Materials Pinch Analysis

achieving a further 3 % reduction in the total amount of water used and an additional 10 % reduction in terms of the amount of effluent generated. It is however in the area of material recovery and reuse where Combined Water and Materials Pinch Analysis outperforms Water Pinch Analysis and much of the additional economic saving is attributable to this.

It may be suggested, given the additional effort required in modelling the system, that Combined Water and Materials Pinch Analysis is an example of an approach yielding diminishing returns, considering the relatively small margin of additional benefit uncovered by the technique. The application of Water Pinch Analysis to the chlor-alkali system however requires a greater level of assumption to make it practicable to the system. While it is noted that the solution provided by Water Pinch Analysis is justified, these assumptions cloud the insight which may be derived from an analysis of the solution. Given that the aim in applying these techniques to industrial systems is to reduce the level of water used and effluent produced by industrial practices, it is the insight provided by the technique which is possibly more valuable than the actual proposed solution. It is thus particularly in this area where the superiority of Combined Water and Materials Pinch Analysis lies.

6.5 THE CONTINUING STUDY

In light of the fact that the chlor-alkali complex at Umbogintwini has ceased operation, the results obtained from this study cannot be implemented on the system on which it is based. It is therefore not considered appropriate to present recommendations for the implementation of the resource-use strategy in the final chapter of this thesis. The possibility does however exist that the results from this study could be implemented on other chlor-alkali complexes. From this perspective, a few considerations related to the continuation of this study are appropriate and are presented as follows:

- It is necessary to simulate the resource-use strategies identified by this study such that effects of factors not included in the Pinch Analysis, for example, trace species and energy, may be quantified. Where required, improvements to the models should be made. The assumption that capital costs are offset by the savings in operating costs similarly needs to be justified.

- The investigation has not considered the introduction of a regeneration process into the system. Given that the marginal values have identified the species which determine the purge flow from the brine circuit, that is, $NaClO_3$ and Na_2SO_4, the introduction of a process capable of reducing the loads of these species in the system should be investigated.

- The cooling circuit subsystem was identified as the subsystem which uses the greatest volume of water and produces the greatest volume of wastewater. This is clearly the area in which benefit would be derived from more accurate modelling, particularly since the pinch constraint arises due to the

representation adopted for the absorption of carbon dioxide from the atmosphere. A further option involves considering both energy and water-use simultaneously; a reduction in the level of evaporation from the system would reduce the amount of water used and effluent generated.

6.6 CONCLUDING REMARKS

In terms of the objectives of this study, this chapter has considered the results obtained from the application of Combined Water and Materials Pinch Analysis to the chlor-alkali complex. In particular, the significance of the pinch as it relates to Combined Water and Materials Pinch Analysis has been discussed and a more general definition of the pinch proposed. As such, the pinch is considered to be that constraint or set of constraints which limits the performance of the system. In this study, the performance of the system was measured in terms of the operating cost. This definition of the pinch thus represents a departure from the normal interpretation of the pinch which is thermodynamically based. The use of marginal values was proposed as a means of identifying process interventions which could bring about further improvement in the performance of the system. These marginal values were used in the analysis of the solution for the chlor-alkali complex and areas where process modifications would be effective were identified. Following the analysis of the results obtained from the optimisation of the subsystems in isolation from each other, an integration strategy was proposed to quantify the performance of the subsystems in combination with each other; a more realistic reflection of the potential savings accruable from the reuse strategy was thus provided. These results were compared to those obtained from the other studies conducted at the chlor-alkali complex. Finally, with the chlor-alkali complex at Umbogintwini having ceased operation, some comments and recommendations on the continuation of this study on other chlor-alkali complexes was presented

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7

CONCLUSIONS

7.1 CONCLUDING REMARKS

This study has involved the application of Pinch Analysis in the identification of the cost optimal strategy for water, reagent and raw material use and effluent generation at the Sasol Polymers chlor-alkali complex located at Umbogintwini, south of Durban. In terms of the original objectives of the study, the following conclusions can be drawn:

- There are three aspects associated with the problem presented by the chlor-alkali complex which make the use of current Water Pinch Analysis tools and theory difficult.

  Firstly, it is difficult to make a clear distinction between the so-called process streams and water streams in the chlor-alkali process system. Current Water Pinch Analysis theory and tools rely on the distinction being made between process streams and water streams. In that framework only the water streams are considered explicitly in the Pinch Analysis; the process streams are represented implicitly through contaminant concentration limits and contaminant mass-load additions to the water streams.

  Secondly, there are raw materials and reagents used by the chlor-alkali process system; reagents are also produced. Given the economic value of these resources, their recovery and reuse is economically desirable and potentially more so than identifying the network configuration which uses the minimum amount of water. The involvement of these resources in the problem manifests itself through the presence of desirable species in the chlor-alkali system. Current Water Pinch Analysis theory does not consider the possibility that species carried by the water may be desirable; only contaminants which are undesirable are considered.

  Finally some of the species present in the chlor-alkali system undergo chemical reactions. Current Water Pinch Analysis theory considers only non-interacting species.

- In developing an approach which is able to deal with the interactions between process streams and water streams, the conceptual definitions of Utility-Water Pinch Analysis and Process-Water Pinch Analysis were introduced. Utility-Water Pinch Analysis is used to describe the existing theory which relies on the process system being segregated into a set of process streams and a set of water streams. Process-Water Pinch Analysis is used to describe the situations where a clear distinction between process streams and water streams cannot be made. While these definitions provide a theoretical framework for the approach required to handle systems in which there are significant interactions between process streams and water streams, they do not include multiple resources. The concept of Combined Water and Materials Pinch Analysis was thus introduced for systems involving water and other resources such as reagents and raw materials. Given that reagents are included in the *materials* category that this approach considers, the approach incorporates the chemical reactions that accompany the use of these reagents

  The approach for Combined Water and Materials Pinch Analysis involves the use of mathematical programming. A superstructure is used to represent the set of possibilities from which the optimal water and materials use strategy is selected. Given that the process operations of the chlor-alkali complex do not conform to any one particular physical structure, the superstructure is formulated in terms of the flow between sources and sinks within the process system. This formulation thus allows it to be applied to any range of process operations, with any number of associated sources and demands. These process operations are subsequently incorporated into the superstructure framework as process modules. A connectivity matrix is used to ensure that only those connections which are realistic possibilities are included in the superstructure. The problem is essentially solved as a nonlinear programming (NLP) problem using standard optimisation tools.

- In applying Combined Water and Materials Pinch Analysis to the chlor-alkali complex, the system was divided into three subsystems which were initially optimised in isolation from each other. These subsystems were subsequently integrated such that the interactions that exist between them could be taken into account. The results from this integration showed that it is possible to reduce the amount of water used by the complex by 14%; the amount of effluent produced by the complex may be reduced by 42%. These improvements in water use and effluent production were accompanied by small improvements in the use of raw materials and reagents by the complex; salt use decreased by 0.2% and caustic soda and hydrochloric acid use decreased by 1.6% and 8.3% respectively. In total, the potential economic saving identified by this study was R 945 727 per annum, based on costs from the year 2000.

- Apart from identifying an optimal resource use strategy, a major attribute of Pinch Analysis is that it yields insight into the performance of a system such that process interventions, which bring further improvement in the use of resources, may be identified. A general definition of the pinch was proposed. According to this definition, the pinch corresponds to that constraint or set of constraints which limits the performance of the system. In the case of Combined Water and Materials Pinch Analysis, the performance of the system is measured in terms of the operating cost. This interpretation of the pinch is thus a departure from the classical thermodynamic interpretation and further relates to a constraint or set of constraints rather than a point. Marginal values present in the solution provided by the optimisation algorithm are used to identify these pinch constraints. These values are also used to identify process interventions which may be effected such that the performance of the system is improved.

- In assessing the suitability of the current techniques to the problem presented by the chlor-alkali complex, several limitations in the existing Water Pinch Analysis theory were identified. While these limitations do exist, it is still possible to apply the current tools and theory to the problem. It is however necessary to include a number of additional constraints in the model such that the theory becomes applicable. Correspondingly, the network configuration identified by this approach will not be as efficient in terms of the use of materials as that identified by the approach which does not require these additional restrictions. As a quantification of this, the application of Water Pinch Analysis to the chlor-alkali complex realised only about 57% of the potential economic savings identified by Combined Water and Materials Pinch Analysis. With the additional constraints included in the Water Pinch Analysis model not having physical justification, the insights yielded by this approach were not as useful as those from Combined Water and Materials Pinch Analysis.

7.2 COMMENTS, RECOMMENDATIONS AND FUTURE WORK

In light of the findings of this study, the following comments, recommendations and areas of future work are noted:

- Two ion-exchange processes are present on the chlor-alkali complex and were considered in the optimisation problem. The optimisation of the demineralisation plant subsystem demonstrated the potential for savings to be identified using Combined Water and Materials Pinch Analysis for ion-exchange processes. The next step in this area of research would be the incorporation of species concentration profiles in the optimisation model. A more detailed investigation into the contaminant species tolerance levels of the

ion-exchange resins should also be conducted. This information would allow more accurate concentration limits to be established for these species at the regenerant inlets to the process. Given that ion-exchange processes are present in many different industries, this area of research has significant application.

- A further application of Combined Water and Materials Pinch Analysis which might be explored is the ability of the approach to screen feeds on the basis of the economics associated with their use. South Africa is known to have a salinity problem and one of the options presently being considered involves the use of effluent brines in the manufacture of chlorine and caustic soda. The methodology would thus prove useful in providing an assessment of the costs involved in the use of these sources.

- This study has favoured the use of marginal values as a means of providing insight into the sensitive areas of the problem; graphical representations, as an alternative approach, were not considered. Such constructions may however be able to yield useful insights into the performance of the system. While it is not known what the exact nature of these constructions would be, there may be a range of constraint specific constructions which might be possible. In this case, the concentration-type composite curves which are already in existence would be one element of this range. Ideally a single construction which is able to represent all types of constraints would be most useful. Of course, such a construction is likely to rely on the identification of a locus from which the optimisation problem appears 1-dimensional.

- Energy considerations are presently excluded from Combined Water and Materials Pinch Analysis. It is likely that this will be one of the important developments of the approach in the near future.

A

MASS-BALANCES

Appendix A presents the reconciled mass-balances for the chlor-alkali complex. Data for these mass-balances was gathered from a number of different sources which included process flow diagrams, operating manuals, physical property data and on-site measurements, amongst others. The balances are considered representative of the activities occurring on the complex and are taken as the absolute basis for the Pinch Analysis which is presented in this thesis. It should be noted however that these balances only consider the species of interest to the Pinch Analysis and certain trace species are absent. The contribution of these species to the overall mass-balance is represented as an equivalent mass of water, which ensures that the sum of the species mass fractions in any stream is unity. Should it be found upon further analysis of the proposed network configurations that these species are of significance, they can be introduced into the balance with the adjustment of the mass fraction of the water.

A further point of note relates to the number of decimal places used to represent the various species mass fractions in the tables presented in this appendix. It is noted that in the brine circuit, for example, concentrations of calcium and magnesium of the order of parts per billion (ppb) are of significance. As such, 1 ppb is equivalent to a mass fraction of 10^{-9}. Other species in the system however have mass fractions of the order of 10^{-1}. Furthermore, the species which are significant at concentrations of the order of ppb also appear in the system at mass fractions of 10^{-2}. With species interacting with each other, mass fractions are seen as the simplest way to track possible mistakes when data is processed, either in the reconciliation or the optimisation. However, this entails the representation of species for which the concentrations are of the order of 10^{-1} to a large number of decimal places. This practice raises two opposing issues. The first one relates to the accuracy of the reconciled data; if the reconciled value of a variable is within 5 % of its true value, consideration of decimal places several orders of magnitude smaller is inappropriate. However, from a computer modelling perspective, it is desirable to have a balanced set of data and one which portrays what is occurring on the plant. In consideration of these issues, the species mass fractions are represented to a large number of decimal places on the understanding that this is done purely to portray the system precisely from a computer modelling point of view. When these numbers are considered from a practical perspective, the accuracy is a lot lower and extends to only a few significant figures.

A.1 THE DEMINERALISATION PLANT

Figure A.1 shows a block diagram of the demineralisation plant. Both the normal cycle of operation and the regeneration cycle of operation are shown.
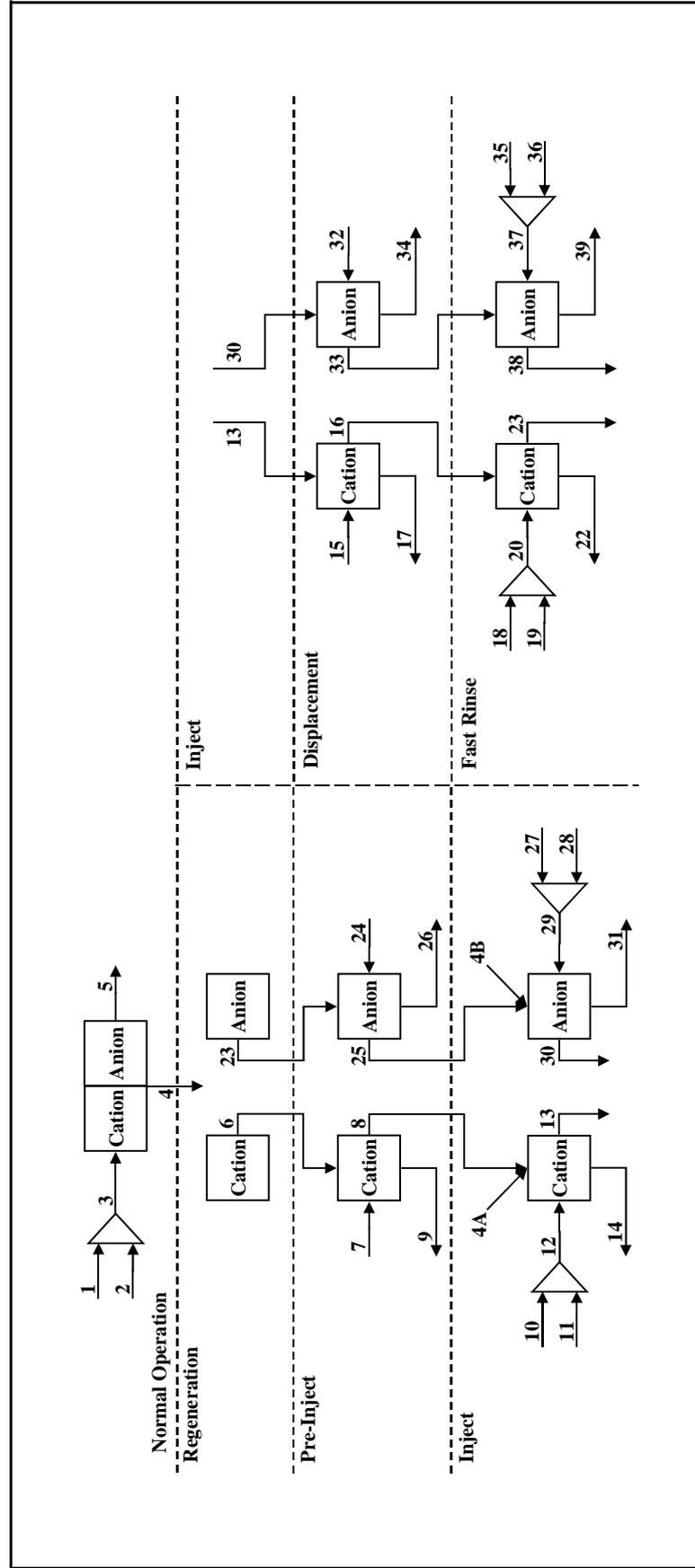
Figure A.1. *Block diagram of the demineralisation plant showing the normal cycle of operation and the regeneration cycle of operation.*

Table A.1. *Reconciled mass-balance for the demineralisation plant reflecting one complete normal cycle of operation, lasting 16 hours, and one regeneration cycle.*

No	Stream Description	Flow [t]	Mass Fraction				
			MgCl$_2$	Na$_2$CO$_3$	Na$_2$SO$_4$	NaClO$_3$	NaCl
1	Umgeni Water to demineralised water production	127.4610	0.0000234998	0.0000027769	0.0000177413	0	0.0000723057
2	Umbogintwini River water to demineralised water production	127.4610	0.0000274228	0.0000145736	0.0000606386	0	0.0000694903
3	Raw water to demineralised water production	254.9220	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
4	Ions (as salts) removed in demineralised water production	0.0484	0.1339882483	0.0456671017	0.2062977369	0	0.3732104439
5	Demineralised water	254.8736	0.0000000078	0	0	0	0
6	Hold-up from normal operation to regeneration - cation bed regeneration	0.8761	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
7	Demineralised water to cation bed regeneration - Pre-Inject	0.0556	0.0000000078	0	0	0	0
8	Hold-up from cation bed regeneration - Pre-Inject	0.8761	0.0000238464	0.0000081249	0.0000367035	0	0.0000663997
9	Effluent from cation bed regeneration to UOS - Pre-Inject	0.0556	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
10	Demineralised water to hydrochloric acid dilution - cation bed regeneration - Inject	2.2235	0.0000000078	0	0	0	0
11	Hydrochloric acid (31% m/m HCl) to hydrochloric acid dilution - cation bed regeneration - Inject	0.3500	0.0000000053	0	0	0	0
12	Dilute hydrochloric acid to cation bed regeneration - Inject	2.5735	0.0000000075	0	0	0	0
13	Hold-up from cation bed regeneration - Inject	0.8928	0.0000000075	0	0	0	0
14	Effluent from cation bed regeneration to UOS - Inject	2.5739	0.0025290777	0.0000027656	0.0000124935	0	0.0111859912
15	Demineralised water to cation bed regeneration - Displacement	5.5588	0.0000000078	0	0	0	0
16	Hold-up from cation bed regeneration - Displacement	0.8761	0.0000000078	0.0000000000	0.0000000000	0	0.0000000000

cont.

Table A.1. *cont.*

No	Stream Description	Flow [t]	Mass Fraction				
			MgCl$_2$	Na$_2$CO$_3$	Na$_2$SO$_4$	NaClO$_3$	NaCl
17	Effluent from cation bed regeneration to UOS - Displacement	5.5754	0.0000000000078	0.0000000000000	0.0000000000000	0	0.0000000000000
18	Umgeni Water to cation bed regeneration - Fast Rinse	1.4934	0.0000234998	0.0000027769	0.0000177413	0	0.0000723057
19	Umbogintwini River water to cation bed regeneration - Fast Rinse	1.4934	0.0000274228	0.0000145736	0.0000606386	0	0.0000694903
20	Raw water to cation bed regeneration - Fast Rinse	2.9868	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
21	Hold-up from cation bed regeneration - Fast Rinse	0.8761	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
22	Effluent from cation bed regeneration - Fast Rinse	2.9868	0.0000179949	0.0000061305	0.0000276942	0	0.0000501013
23	Hold-up from normal operation to regeneration - anion bed regeneration	0.8761	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
24	Demineralised water to anion bed regeneration - Pre-Inject	0.0556	0.0000000000078	0	0	0	0
25	Hold-up from anion bed regeneration - Pre-Inject	0.8761	0.0000238464	0.0000081249	0.0000367035	0	0.0000663997
26	Effluent from anion bed regeneration to UOS - Pre-Inject	0.0556	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
27	Demineralised water to caustic soda dilution - anion bed regeneration- Inject	2.2235	0.0000000000078	0	0	0	0
28	Caustic soda (32% m/m NaOH) to caustic soda dilution - anion bed regeneration - Inject	0.3900	0.0000000000004	0.0034139200	0.0011060000	0.0000150959	0.0000539022
29	Dilute caustic soda to anion bed regeneration - Inject	2.6135	0.0000000000067	0.0005094415	0.0001650426	0.0000022527	0.0000080435
30	Hold-up from anion bed regeneration - Inject	0.9161	0.0000000000067	0.0005094415	0.0001650426	0.0000022527	0.0000080435
31	Effluent from anion bed regeneration to UOS - Inject	2.5913	0.0000080668	0.0011898814	0.0039758200	0.0000014756	0.0129429809
32	Demineralised water to anion bed regeneration - Displacement	5.5588	0.0000000000078	0.0000000000000	0.0000000000000	0	0.0000000000000

cont.

Table A.1. *cont.*

| | | | Mass Fraction | | | | |
No	Stream Description	Flow [t]	MgCl₂	Na₂CO₃	Na₂SO₄	NaClO₃	NaCl
33	Hold-up from anion bed regeneration - Displacement	0.8761	0.0000000000078	0	0	0	0
34	Effluent from anion bed regeneration to UOS - Displacement	5.5987	0.0000000077	0.0000833558	0.0000270046	0.0000003686	0.0000013161
35	Umgeni Water to anion bed regeneration - Fast Rinse	1.4934	0.0000234998	0.0000027769	0.0000177413	0	0.0000723057
36	Umbogintwini River water to anion bed regeneration - Fast Rinse	1.4934	0.0000274228	0.0000145736	0.0000606386	0	0.0000694903
37	Raw water to anion bed regeneration - Fast Rinse	2.9868	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
38	Hold-up from anion bed regeneration - Fast Rinse	0.8761	0.0000254613	0.0000086753	0.0000391899	0	0.0000708980
39	Effluent from anion bed regeneration - Fast Rinse	2.9868	0.0000179949	0.0000061305	0.0000276942	0	0.0000501013

cont.

Table A.1. *cont.*

| | | Mass Fraction | | | | | |
No	Stream Description	CaCl₂	Cl₂	H₂O	HCl	NaOH	INSOLS
1	Umgeni Water to demineralised water production	0.0000138511	0	0.9998577722	0	0	0.0000120530
2	Umbogintwini River water to demineralised water production	0.0000415421	0	0.9997622265	0	0	0.0000241061
3	Raw water to demineralised water production	0.0000276966	0	0.9998099993	0	0	0.0000180796
4	Ions (as salts) removed in demineralised water production	0.1456648453	0	0	0	0	0.0951716240
5	Demineralised water	0.0000000249	0	0.9999999672	0	0	0
6	Hold-up from normal operation to regeneration - cation bed regeneration	0.0000276966	0	0.9998099993	0	0	0.0000180796

cont.

Table A.1. *cont.*

No	Stream Description	Mass Fraction					
		CaCl$_2$	Cl$_2$	H$_2$O	HCl	NaOH	INSOLS
7	Demineralised water to cation bed regeneration - Pre-Inject	0.0000000249	0	0.9999999672	0	0	0.0000000000
8	Hold-up from cation bed regeneration - Pre-Inject	0.0000259409	0	0.9998220522	0	0	0.0000169325
9	Effluent from cation bed regeneration to UOS - Pre-Inject	0.0000276966	0	0.9998099993	0	0	0.0000180796
10	Demineralised water to hydrochloric acid dilution - cation bed regeneration - Inject	0.0000000249	0	0.9999999672	0	0	0.0000000000
11	Hydrochloric acid (31% m/m HCl) to hydrochloric acid dilution - cation bed regeneration - Inject	0.0000000170	0.0000047262	0.6851847367	0.3148105148	0	0
12	Dilute hydrochloric acid to cation bed regeneration - Inject	0.0000000238	0.0000006428	0.9571847175	0.0428146084	0	0.0000000000
13	Hold-up from cation bed regeneration - Inject	0.0000000238	0.0000006428	0.9571847175	0.0428146084	0	0
14	Effluent from cation bed regeneration to UOS - Inject	0.0027494936	0.0000004197	0.9653572852	0.0172613944	0	0.0009010789
15	Demineralised water to cation bed regeneration - Displacement	0.0000000249	0	0.9999999672	0	0	0.0000000000
16	Hold-up from cation bed regeneration - Displacement	0.0000000249	0	0.9999999672	0	0	0
17	Effluent from cation bed regeneration to UOS - Displacement	0.0000000247	0.0000001029	0.9931439199	0.0068559446	0	0
18	Umgeni Water to cation bed regeneration - Fast Rinse	0.0000138511	0.0000000000	0.9998577722	0.0000000000	0	0.000012053
19	Umbogintwini River water to cation bed regeneration - Fast Rinse	0.0000415421	0.0000000000	0.9997622265	0.0000000000	0	0.0000241061
20	Raw water to cation bed regeneration - Fast Rinse	0.0000276966	0.0000000000	0.9998099993	0.0000000000	0	0.0000180796
21	Hold-up from cation bed regeneration - Fast Rinse	0.0000276966	0	0.9998099993	0	0	0.0000180796
22	Effluent from cation bed regeneration - Fast Rinse	0.0000000000	0	0.9998657233	0	0	0.0000127762

cont.

Table A.1. *cont.*

No	Stream Description	CaCl$_2$	Cl$_2$	H$_2$O	HCl	NaOH	INSOLS
23	Hold-up from normal operation to regeneration - anion bed regeneration	0.0000276966		0.9998099993	0	0	0.0000180796
24	Demineralised water to anion bed regeneration - Pre-Inject	0.0000000249		0.9999999672	0	0	0
25	Hold-up from anion bed regeneration - Pre-Inject	0.0000259409		0.9998220522	0	0	0.0000169325
26	Effluent from anion bed regeneration to UOS - Pre-Inject	0.0000276966		0.9998099993	0	0	0.0000180796
27	Demineralised water to caustic soda dilution - anion bed regeneration- Inject	0.0000000249		0.9999999672	0	0	0
28	Caustic soda (32% m/m NaOH) to caustic soda dilution - anion bed regeneration - Inject	0.0000000014		0.6798367297	0	0.315743503	0
29	Dilute caustic soda to anion bed regeneration - Inject	0.0000000214		0.9522236733	0	0.0470915182	0
30	Hold-up from anion bed regeneration - Inject	0.0000000214		0.9522236733	0	0.0470915182	0
31	Effluent from anion bed regeneration to UOS - Inject	0.0000087846		0.9617854804	0	0.0191924998	0.0008950105
32	Demineralised water to anion bed regeneration - Displacement	0.0000000249		0.9999999672	0	0	0
33	Hold-up from anion bed regeneration - Displacement	0.0000000249		0.9999999672	0	0	0
34	Effluent from anion bed regeneration to UOS - Displacement	0.0000000243		0.9921827186	0	0.0077052044	0
35	Umgeni Water to anion bed regeneration - Fast Rinse	0.0000138511		0.9998577722	0	0	0.0000120530
36	Umbogintwini River water to anion bed regeneration - Fast Rinse	0.0000415421		0.9997622265	0	0	0.0000241061
37	Raw water to anion bed regeneration - Fast Rinse	0.0000276966		0.9998099993	0	0	0.0000180796
38	Hold-up from anion bed regeneration - Fast Rinse	0.0000276966		0.9998099993	0	0	0.0000180796
39	Effluent from anion bed regeneration - Fast Rinse	0.0000195795		0.9998657233	0	0	0.0000127762

Table A.1. *cont.*

No	Stream Description	Flow [t]	Mass Fraction			
			Na⁺	Ca²⁺	Mg²⁺	INSOLS
4A	Cations removed in demineralised water production	0.0178	0.6345849019	0.1430210520	0.0930152257	0.1293788204

cont.

Table A.1. *cont.*

No	Stream Description	Flow [t]	Mass Fraction			
			Cl⁻	CO₃²⁻	SO₄²⁻	INSOLS
4B	Anions removed in demineralised water production	0.0306	0.6631426182	0.0408986704	0.2206882655	0.0752704460

A.2 THE BRINE CIRCUIT

Figure A.2 shows a block diagram of the brine circuit, together with the chlorine gas processing operations, the hydrogen gas processing operations and the caustic evaporators. Both the normal cycle of operation of the ion-exchanger and the regeneration cycle are included in the diagram.

Figure A.2. *Block diagram of the brine circuit, together with the chlorine gas processing operations, the hydrogen gas processing operations and the caustic evaporators. Both the normal cycle of operation and the regeneration cycle of operation of the ion-exchanger are shown.*

Table A.2. *Reconciled mass-balance for the brine circuit, including the chlorine gas processing operations, the hydrogen gas processing operations and the caustic evaporators. Both cycles of operation for the ion-exchanger are included in the mass-balance.*

No	Stream Description	Flow [kg/h]	MgCl$_2$	Na$_2$CO$_3$	NaHSO$_3$	Na$_2$SO$_4$	NaClO$_3$
				Mass Fraction			
1	Oxygen for destruction of residual NaHSO$_3$ in lean brine	0.3742	0	0	0	0	0
2	Lean brine to resaturator - NaHSO$_3$ destroyed	48825.3602	0.0000000400	0.0000554846	0	0.0066550060	0.0057693170
3	Raw salt to resaturator	5956.4858	0.0010784250	0.0002950220	0	0.0015975570	0
4	Brine to calcium precipitation	54781.8460	0.0001172940	0.0000815298	0	0.0061051040	0.0051420140
5	Demineralised water to sodium carbonate dilution	221.8024	0.0000000078	0	0	0	0
6	Solid sodium carbonate to sodium carbonate dilution	43.9861	0	0.9800000000	0	0.0004000000	0
7	Dilute sodium carbonate to calcium precipitation	265.7885	0.0000000065	0.1621829740	0	0.0000661971	0
8	Brine from calcium precipitation	55047.6345	0.0001167280	0.0007762900	0	0.0060759460	0.0051171860
9	Brine from brine filter backwash	4177.0791	0.0000906020	0.0007714120	0	0.0060234460	0.0050724580
10	Brine to magnesium precipitation	59224.7135	0.0001148850	0.0007759460	0	0.0060722430	0.0051140320
11	Demineralised water to caustic soda dilution - magnesium precipitation	23.3795	0.0000000078	0	0	0	0
12	Caustic soda (32% m/m NaOH) to caustic soda dilution - magnesium precipitation	31.0405	0.0000000004	0.0034139200	0	0.0011060000	0.00000150959
13	Dilute caustic soda to magnesium precipitation	54.4200	0.0000000036	0.0019472610	0	0.0006308500	0.0000086105
14	Brine from magnesium precipitation	59279.1335	0.0000075778	0.0007770210	0	0.0060672480	0.0051093450
15	Flocculant addition to brine	278.7680	0.0000000078	0	0	0	0
16	Brine to clarification	59557.9015	0.0000075424	0.0007733850	0	0.0060388490	0.0050854300
17	Brine sludge	106.3169	0.0000069100	0.0007085380	0	0.0055325020	0.0046590250

cont.

Table A.2. *cont.*

No	Stream Description	Flow [kg/h]	Mass Fraction				
			$MgCl_2$	Na_2CO_3	$NaHSO_3$	Na_2SO_4	$NaClO_3$
18	Brine to brine filter (primary filtration)	59451.5846	0.0000075435	0.0007735010	0	0.0060397550	0.0050861920
19	Removed material from brine filter (primary filtration)	1.4572	0.2584648940	0	0	0	0
20	Filtered brine from brine filter (primary filtration)	59450.1274	0.0000012084	0.0007735190	0	0.0060399030	0.0050863170
21	Alpha-cellulose addition to filtered brine	142.0000	0.0000000078	0	0	0	0
22	Filtered brine to polishing filter (secondary filtration)	59592.1274	0.0000012055	0.0007716760	0	0.0060255110	0.0050741970
23	Removed material from polishing filter (secondary filtration)	0.3659	0.1255030970	0	0	0	0
24	Filtered brine from polishing filter (secondary filtration)	59591.7615	0.0000004349	0.0007716810	0	0.0060255480	0.0050742280
25	Filtered brine to brine filter backwash	4175.6219	0.0000004349	0.0007716810	0	0.0060255480	0.0050742280
26	Filtered brine from polishing filter to ion-exchange	55280.2662	0.0000004349	0.0007716810	0	0.0060255480	0.0050742280
27	Hold-up of filtered brine to ion-exchange regeneration - Brine Displacement stage (IXR1)	53.0238	0.0000004349	0.0007716810	0	0.0060255480	0.0050742280
28	Filtered brine to ion-exchange regeneration - Brine Replacement stage (IXR7)	82.8496	0.0000004349	0.0007716810	0	0.0060255480	0.0050742280
29	Demineralised water to ion-exchange regeneration - Brine Displacement stage (IXR1)	221.2444	0.0000000078	0	0	0	0
30	Effluent from ion-exchange regeneration - Brine Displacement stage (IXR1)	230.0193	0.0000001063	0.0001778870	0	0.0013890020	0.0011697050

cont.

Table A.2. *cont.*

| No | Stream Description | Flow [kg/h] | Mass Fraction | | | | | |
			MgCl$_2$	Na$_2$CO$_3$	NaHSO$_3$	Na$_2$SO$_4$	NaClO$_3$
31	Hold-up from ion-exchange regeneration - Brine Displacement stage (IXR1)	44.2489	0.0000000078	0	0	0	0
32	Demineralised water to ion-exchange regeneration - Backwash stage (IXR2)	193.5889	0.0000000078	0	0	0	0
33	Effluent from ion-exchange regeneration - Backwash stage (IXR2)	193.5889	0.0000000078	0	0	0	0
34	Hold-up from ion-exchange regeneration - Backwash stage (IXR2)	44.2489	0.0000000078	0	0	0	0
35	Demineralised water to hydrochloric acid dilution - ion-exchange regeneration	69.3234	0.0000000078	0	0	0	0
36	Hydrochloric acid (31% m/m HCl) to hydrochloric acid dilution - ion-exchange regeneration	19.8220	0.0000000053	0	0	0	0
37	Dilute hydrochloric acid to ion-exchange regeneration - Acid Regeneration stage (IXR3)	89.1454	0.0000000073	0	0	0	0
38	Effluent from ion-exchange regeneration - Acid Regeneration stage (IXR3)	87.6968	0.0002517210	0	0	0	0
39	Ca and Mg ions from ion-exchange to ion-exchange regeneration - Acid Regeneration stage (IXR3)	0.1229	0	0	0	0	0
40	Hold-up from ion-exchange regeneration - Acid Regeneration stage (IXR3)	45.6424	0.0000000073	0	0	0	0

Table A.2. *cont.*

No	Stream Description	Flow [kg/h]	Mass Fraction				
			MgCl₂	Na₂CO₃	NaHSO₃	Na₂SO₄	NaClO₃
41	Hydrogen cation transfer from Acid Regeneration stage (IXR3) to Caustic Regeneration stage (IXR5)	0.0111	0	0	0	0	0
42	Demineralised water to ion-exchange regeneration - Acid Rinse stage (IXR4)	221.2444	0.0000000078	0	0	0	0
43	Hold-up from ion-exchange regeneration - Acid Rinse stage (IXR4)	44.2489	0.0000000078	0	0	0	0
44	Effluent from ion-exchange regeneration - Acid Rinse stage (IXR4)	222.6380	0.0000000077	0	0	0	0
45	Demineralised water to caustic soda dilution - ion-exchange regeneration	100.3159	0.0000000078	0	0	0	0
46	Caustic soda (32% m/m NaOH) to caustic soda dilution - ion-exchange regeneration	14.5610	0.0000000004	0.0034139200	0	0.0011060000	0.0000150959
47	Dilute caustic soda to ion-exchange regeneration - Caustic Regeneration stage (IXR5)	114.8769	0.0000000069	0.0004327250	0	0.0001401890	0.0000019134
48	Sodium cation transfer from Caustic Regeneration stage to ion-exchange	0.2534	0	0	0	0	0
49	Effluent from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	112.9327	0.0000000073	0.0002641050	0	0.0000855613	0.0000011678
50	Hold-up from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	45.9508	0.0000000069	0.0004327250	0	0.0001401890	0.0000019134

cont.

Table A.2. *cont.*

No	Stream Description	Flow [kg/h]	Mass Fraction				
			$MgCl_2$	Na_2CO_3	$NaHSO_3$	Na_2SO_4	$NaClO_3$
51	Demineralised water to ion-exchange regeneration - Caustic Rinse stage (IXR6)	221.2444	0.0000000078	0	0	0	0
52	Effluent from ion-exchange regeneration - Caustic Rinse stage (IXR6)	222.9463	0.0000000076	0.0000891875	0	0.0000288939	0.0000003944
53	Hold-up from ion-exchange regeneration - Caustic Rinse stage (IXR6)	44.2489	0.0000000078	0	0	0	0
54	Effluent from ion-exchange regeneration - Brine Replacement stage (IXR7)	74.0748	0.0000001798	0.0003107140	0	0.0024261600	0.0020431150
55	Hold-up from ion-exchange regeneration - Brine Replacement stage (IXR7)	53.0238	0.0000004349	0.0007716810	0	0.0060255480	0.0050742280
56	Brine to ion-exchange	55333.2900	0.0000004349	0.0007716810	0	0.0060255480	0.0050742280
57	Ultrapure brine to electrolyser	55333.4205	0.0000000359	0.0007716790	0	0.0060255340	0.0050742160
58	Demineralised water to caustic soda dilution - electrolyser	4110.1569	0.0000000078	0	0	0	0
59	Dilute caustic soda to electrolyser	64225.6800	0.0000000005	0.0031954440	0	0.0010352210	0.0000141298
60	Caustic soda (32% m/m NaOH) from electrolyser	71898.2038	0.0000000004	0.0034139200	0	0.0011060000	0.0000150959
61	Caustic soda (32% m/m NaOH) from electrolyser for internal use	2902.9818	0.0000000004	0.0034139200	0	0.0011060000	0.0000150959
62	Caustic soda (32% m/m NaOH) to caustic evaporation	8879.6990	0.0000000004	0.0034139200	0	0.0011060000	0.0000150959
63	Caustic soda (32% m/m NaOH) to caustic soda dilution - electrolyser	60115.5231	0.0000000004	0.0034139200	0	0.0011060000	0.0000150959
64	Caustic soda (50% m/m NaOH) from caustic evaporation	5604.4105	0.0000000007	0.0054090580	0	0.0017523600	0.0000239181
65	Wet hydrogen gas from electrolyser to hydrogen cooler	974.8138	0.0000000000	0	0	0	0

cont.

Table A.2. *cont.*

			Mass Fraction				
No	Stream Description	Flow [kg/h]	$MgCl_2$	Na_2CO_3	$NaHSO_3$	Na_2SO_4	$NaClO_3$
66	Wet chlorine gas from electrolyser to chlorine cooler	4108.3921	0	0	0	0	0
67	Lean brine from electrolyser	42577.6907	0.0000000467	0.0000581177	0	0.0075246390	0.0069418520
68	Hydrochloric acid (31% m/m HCl) to primary dechlorination	279.2837	0.0000000053	0	0	0	0
69	Chlorinated condensate from chlorine cooler	788.5239	0	0	0	0	0
70	Lean brine to primary dechlorination	43645.4983	0.0000000456	0.0000566958	0	0.0073405450	0.0067720170
71	Waste gas to sodium hypochlorite synthesis	195.1306	0	0	0	0	0
72	Lean brine to secondary dechlorination	43450.3677	0.0000000458	0.0000569504	0	0.0073735100	0.0068024290
73	Demineralised water to caustic soda dilution - secondary dechlorination	81.1966	0.0000000078	0	0	0	0
74	Caustic soda (32% m/m NaOH) to caustic soda dilution - secondary dechlorination	107.8034	0.0000000004	0.0034139200	0	0.0011060000	0.0000150959
75	Dilute caustic soda to secondary dechlorination	189.0000	0.0000000036	0.0019472610	0	0.0006308500	0.0000086105
76	Demineralised water to sodium bisulphite dilution	134.7939	0.0000000078	0	0	0	0
77	Sodium bisulphite powder to sodium bisulphite dilution	14.9771	0.0000000000	0	1	0	0
78	Dilute sodium bisulphite to secondary dechlorination	149.7710	0.0000000070	0	0.1000000000	0	0
79	Dilute sodium bisulphite and dilute caustic soda to secondary dechlorination	338.7710	0.0000000051	0.0010863750	0.0442101010	0.0003519500	0.0000048038
80	Lean brine from secondary dechlorination	43789.1387	0.0000000455	0.0000649145	0.0000583220	0.0077064460	0.0067498400
81	Lean brine purge	2056.4450	0.0000000455	0.0000649145	0.0000583220	0.0077064460	0.0067498400

cont.

Table A.2. *cont.*

No	Stream Description	Flow [kg/h]	Mass Fraction				
			MgCl$_2$	Na$_2$CO$_3$	NaHSO$_3$	Na$_2$SO$_4$	NaClO$_3$
82	Lean brine to water make-up	41732.6937	0.0000000000455	0.0000649145	0.0000583220	0.0077064460	0.0067498400
83	Demineralised water to water make-up	1087.0685	0.0000000000078	0	0	0	0
84	Condensate from caustic evaporation	3275.2885	0	0	0	0	0
85	Steam condensate from caustic evaporation	2729.9350	0	0	0	0	0
86	Ca and Mg load correction for condensate from caustic evaporation	0.0002	0.2391394040	0	0	0	0
87	Condensate to water make-up	6005.2237	0.0000000000078	0	0	0	0
88	Condensate from hydrogen cooler to drain	831.6596	0	0	0	0	0
89	Hydrogen gas from hydrogen cooler	143.1542	0	0	0	0	0
90	Hydrogen gas for Internal use	65.4554	0	0	0	0	0
91	Hydrogen gas to hydrogen chiller	77.6988	0	0	0	0	0
92	Condensate from hydrogen chiller to drain	18.8391	0	0	0	0	0
93	Dry hydrogen gas to Alliance Peroxide	58.8596	0	0	0	0	0
94	Lean brine to Resaturator - residual NaHSO$_3$ present	48824.9859	0.0000000000400	0.0000554850	0.0000498502	0.0065870110	0.0057693620
95	Chlorine gas from chlorine cooler	3319.8683	0	0	0	0	0
96	Water removed from chlorine gas by sulphuric acid drying	47.1494	0	0	0	0	0
97	Dry chlorine gas	3272.7189	0	0	0	0	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction					
		NaOCl	NaCl	Mg(OH)$_2$	CaCl$_2$	Cl$_2$	H$_2$O
1	Oxygen for destruction of residual NaHSO$_3$ in lean brine	0	0	0	0	0	0
2	Lean brine to resaturator - NaHSO$_3$ destroyed	0	0.1655384630	0	0.0000000333	0.0000034282	0.8217055250
3	Raw salt to resaturator	0	0.9779000570	0	0.0009394910	0	0.0180910980
4	Brine to calcium precipitation	0	0.2538673650	0	0.0001021820	0.0000030554	0.7343277120
5	Demineralised water to sodium carbonate dilution	0	0	0	0.0000000249	0	0.9999999670
6	Solid sodium carbonate to sodium carbonate dilution	0	0	0	0	0	0.0196000000
7	Dilute sodium carbonate to calcium precipitation	0	0	0	0.0000000208	0	0.8377508010
8	Brine from calcium precipitation	0	0.2527385660	0	0.0000096242	0.0000030407	0.7348270730
9	Brine from brine filter backwash	0	0.2506695150	0	0.0001507220	0.0000030141	0.7367849520
10	Brine to magnesium precipitation	0	0.2525926370	0	0.0000195757	0.0000030388	0.7349651610
11	Demineralised water to caustic soda dilution - magnesium precipitation	0	0	0	0.0000000249	0	0.9999999670
12	Caustic soda (32% m/m NaOH) to caustic soda dilution - magnesium precipitation	0	0.0000539022	0	0.0000000014	0	0.6798367300
13	Dilute caustic soda to magnesium precipitation	0	0.0000307452	0	0.0000000115	0	0.8173825190
14	Brine from magnesium precipitation	0	0.2524923750	0.0000656687	0.0000195577	0.0000030360	0.7350408220
15	Flocculant addition to brine	0	0.0000000000	0	0.0000000249	0	0.9999999670
16	Brine to clarification	0	0.2513105530	0.0000653613	0.0000194663	0.0000030218	0.7362809960
17	Brine sludge	0	0.2302385890	0.0366148760	0.0000178341	0.0000027684	0.6745450810

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction					
		NaOCl	NaCl	Mg(OH)$_2$	CaCl$_2$	Cl$_2$	H$_2$O
18	Brine to brine filter (primary filtration)	0	0.2513482360	0	0.0000194692	0.0000030222	0.7363913980
19	Removed material from brine filter (primary filtration)	0	0	0	0.4151455650	0	0
20	Filtered brine from brine filter (primary filtration)	0	0.2513543970	0	0.0000092939	0.0000030223	0.7364094480
21	Alpha-cellulose addition to filtered brine	0	0	0	0.0000000249	0	0.9999999670
22	Filtered brine to polishing filter (secondary filtration)	0	0.2507554530	0	0.0000092719	0.0000030151	0.7370375490
23	Removed material from polishing filter (secondary filtration)	0	0	0	0.5495561150	0	0
24	Filtered brine from polishing filter (secondary filtration)	0	0.2507569930	0	0.0000058974	0.0000030151	0.7370420740
25	Filtered brine to brine filter backwash	0	0.2507569930	0	0.0000058974	0.0000030151	0.7370420740
26	Filtered brine from polishing filter to ion-exchange	0	0.2507569930	0	0.0000058974	0.0000030151	0.7370420740
27	Hold-up of filtered brine to ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0.2507569930	0	0.0000058974	0.0000030151	0.7370420740
28	Filtered brine to ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0.2507569930	0	0.0000058974	0.0000030151	0.7370420740
29	Demineralised water to ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0.0000000249	0	0.9999999670
30	Effluent from ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0.0578041920	0	0.0000013786	0.0000006950	0.9393832390

cont.

Table A.2. *cont.*

No	Stream Description	NaOCl	NaCl	Mg(OH)₂	CaCl₂	Cl₂	H₂O
31	Hold-up from ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0.0000000249	0	0.9999999670
32	Demineralised water to ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0.0000000249	0	0.9999999670
33	Effluent from ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0.0000000249	0	0.9999999670
34	Hold-up from ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0.0000000249	0	0.9999999670
35	Demineralised water to hydrochloric acid dilution - ion-exchange regeneration	0	0	0	0.0000000249	0	0.9999999670
36	Hydrochloric acid (31% m/m HCl) to hydrochloric acid dilution - ion-exchange regeneration	0	0	0	0.0000000170	0.0000047262	0.6851847370
37	Dilute hydrochloric acid to ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0.0000000232	0.0000010509	0.9299989190
38	Effluent from ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0.0037038730	0.0000005213	0.9659024830
39	Ca and Mg ions from ion-exchange to ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0	0	0
40	Hold-up from ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0.0000000232	0.0000010509	0.9299989190

cont.

Table A.2. *cont.*

		Mass Fraction					
No	Stream Description	NaOCl	NaCl	Mg(OH)$_2$	CaCl$_2$	Cl$_2$	H$_2$O
41	Hydrogen cation transfer from Acid Regeneration stage (IXR3) to Caustic Regeneration stage (IXR5)	0	0	0	0	0	0
42	Demineralised water to ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0.0000000249	0	0.9999999670
43	Hold-up from ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0.0000000249	0	0.9999999670
44	Effluent from ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0.0000000246	0.0000002154	0.9856492360
45	Demineralised water to caustic soda dilution - ion-exchange regeneration	0	0	0	0.0000000249	0	0.9999999670
46	Caustic soda (32% m/m NaOH) to caustic soda dilution - ion-exchange regeneration	0	0.0000539022	0	0.0000000014	0	0.6798367300
47	Dilute caustic soda to ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0.0000068323	0	0.0000000219	0	0.9594183120
48	Sodium cation transfer from Caustic Regeneration stage to ion-exchange	0	0	0	0	0	0
49	Effluent from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0.0000041699	0	0.0000000232	0	0.9791357870
50	Hold-up from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0.0000068323	0	0.0000000219	0	0.9594183120

Table A.2. *cont.*

No	Stream Description	Mass Fraction					
		NaOCl	NaCl	Mg(OH)$_2$	CaCl$_2$	Cl$_2$	H$_2$O
51	Demineralised water to ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0.0000000249	0	0.9999999670
52	Effluent from ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0.00000014082	0	0.0000000243	0	0.9916358090
53	Hold-up from ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0.0000000249	0	0.9999999670
54	Effluent from ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0.1009661820	0	0.0000023895	0.0000012140	0.8941211480
55	Hold-up from ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0.2507569930	0	0.0000058974	0.0000030151	0.7370420740
56	Brine to ion-exchange	0	0.2507569930	0	0.0000058974	0.0000030151	0.7370420740
57	Ultrapure brine to electrolyser	0	0.2507680440	0	0.0000000273	0	0.7370403360
58	Demineralised water to caustic soda dilution - electrolyser	0	0	0	0.0000000249	0	0.9999999670
59	Dilute caustic soda to electrolyser	0	0.0000504527	0	0.0000000016	0	0.7003257500
60	Caustic soda (32% m/m NaOH) from electrolyser	0	0.0000539022	0	0.0000000014	0	0.6798367300
61	Caustic soda (32% m/m NaOH) from electrolyser for internal use	0	0.0000539022	0	0.0000000014	0	0.6798367300
62	Caustic soda (32% m/m NaOH) to caustic evaporation	0	0.0000539022	0	0.0000000014	0	0.6798367300
63	Caustic soda (32% m/m NaOH) to caustic soda dilution - electrolyser	0	0.0000539022	0	0.0000000014	0	0.6798367300
64	Caustic soda (50% m/m NaOH) from caustic evaporation	0	0.0000854034	0	0.0000000023	0	0.4927292600
65	Wet hydrogen gas from electrolyser to hydrogen cooler	0	0	0	0	0	0.8965839710

cont.

Table A.2. *cont.*

| No | Stream Description | Mass Fraction | | | | | |
		NaOCl	NaCl	Mg(OH)$_2$	CaCl$_2$	Cl$_2$	H$_2$O
66	Wet chlorine gas from electrolyser to chlorine cooler	0	0	0	0	0.7921640310	0.2023507890
67	Lean brine from electrolyser	0.0020000000	0.1971187910	0	0.0000000355	0.0006008860	0.7857512390
68	Hydrochloric acid (31% m/m HCl) to primary dechlorination	0	0	0	0.0000000170	0.0000047262	0.6851847370
69	Chlorinated condensate from chlorine cooler	0	0	0	0	0.0055000000	0.9945000000
70	Lean brine to primary dechlorination	0	0.1938312790	0	0.0000000347	0.0025480330	0.7893523060
71	Waste gas to sodium hypochlorite synthesis	0	0	0	0.0000000000	0.5256457240	0.4743542760
72	Lean brine to secondary dechlorination	0	0.1947017530	0	0.0000000348	0.0001988620	0.7907669250
73	Demineralised water to caustic soda dilution - secondary dechlorination	0	0	0	0.0000000249	0	0.9999999670
74	Caustic soda (32% m/m NaOH) to caustic soda dilution - secondary dechlorination	0	0.0000539022	0	0.0000000014	0	0.6798367300
75	Dilute caustic soda to secondary dechlorination	0	0.0000307452	0	0.0000000115	0	0.8173825190
76	Demineralised water to sodium bisulphite dilution	0	0	0	0.0000000249	0	0.9999999670
77	Sodium bisulphite powder to sodium bisulphite dilution	0	0	0	0.0000000000	0	0.0000000000
78	Dilute sodium bisulphite to secondary dechlorination	0	0	0	0.0000000224	0	0.8999999710
79	Dilute sodium bisulphite and dilute caustic soda to secondary dechlorination	0	0.0000171527	0	0.0000000163	0	0.8539077770
80	Lean brine from secondary dechlorination	0	0.1936724980	0	0.0000000347	0.0000040108	0.7914024220
81	Lean brine purge	0	0.1936724980	0	0.0000000347	0.0000040108	0.7914024220

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction					
		NaOCl	NaCl	Mg(OH)$_2$	CaCl$_2$	Cl$_2$	H$_2$O
82	Lean brine to water make-up	0	0.1936724980	0	0.0000000347	0.0000040108	0.7914024220
83	Demineralised water to water make-up	0	0	0	0.0000000249	0	0.9999999670
84	Condensate from caustic evaporation	0	0	0	0	0	1
85	Steam condensate from caustic evaporation	0	0	0	0	0	1
86	Ca and Mg load correction for condensate from caustic evaporation	0	0	0	0.7608605960	0	0
87	Condensate to water make-up	0	0	0	0.0000000249	0	0.9999999670
88	Condensate from hydrogen cooler to drain	0	0	0	0	0	1
89	Hydrogen gas from hydrogen cooler	0	0	0	0	0	0.2957846580
90	Hydrogen gas for Internal use	0	0	0	0	0	0.2957846580
91	Hydrogen gas to hydrogen chiller	0	0	0	0	0	0.2957846580
92	Condensate from hydrogen chiller to drain	0	0	0	0	0	1
93	Dry hydrogen gas to Alliance Peroxide	0	0	0	0	0	0.0703872360
94	Lean brine to Resaturator - residual NaHSO$_3$ present	0	0.1655397310	0	0.0000000333	0.0000034282	0.8217031930
95	Chlorine gas from chlorine cooler	0	0	0	0	0.9790098060	0.0142021920
96	Water removed from chlorine gas by sulphuric acid drying	0	0	0	0	0	1
97	Dry chlorine gas	0	0	0	0	0.9931142050	0

cont.

Table A.2. *cont.*

		Mass Fraction				
No	Stream Description	H_2	O_2	HCl	NaOH	$CaCO_3$
1	Oxygen for destruction of residual $NaHSO_3$ in lean brine	0	1	0	0	0
2	Lean brine to resaturator - $NaHSO_3$ destroyed	0	0	0	0.0002727030	0
3	Raw salt to resaturator	0	0	0	0	0
4	Brine to calcium precipitation	0	0	0	0.0002430520	0
5	Demineralised water to sodium carbonate dilution	0	0	0	0	0
6	Solid sodium carbonate to sodium carbonate dilution	0	0	0	0	0
7	Dilute sodium carbonate to calcium precipitation	0	0	0	0	0
8	Brine from calcium precipitation	0	0	0	0.0002418780	0.0000830257
9	Brine from brine filter backwash	0	0	0	0.0003200170	0
10	Brine to magnesium precipitation	0	0	0	0.0002473890	0.0000771700
11	Demineralised water to caustic soda dilution - magnesium precipitation	0	0	0	0	0
12	Caustic soda (32% m/m NaOH) to caustic soda dilution - magnesium precipitation	0	0	0	0.3155743500	0
13	Dilute caustic soda to magnesium precipitation	0	0	0	0.1800000000	0
14	Brine from magnesium precipitation	0	0	0	0.0003223440	0.0000770991
15	Flocculant addition to brine	0	0	0	0	0
16	Brine to clarification	0	0	0	0.0003208350	0.0000767382
17	Brine sludge	0	0	0	0.0002939340	0.0429881590

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		H₂	O₂	HCl	NaOH	CaCO₃
18	Brine to brine filter (primary filtration)	0	0	0	0.0003208830	0
19	Removed material from brine filter (primary filtration)	0	0	0	0	0
20	Filtered brine from brine filter (primary filtration)	0	0	0	0.0003208910	0
21	Alpha-cellulose addition to filtered brine	0	0	0	0	0
22	Filtered brine to polishing filter (secondary filtration)	0	0	0	0.0003201270	0
23	Removed material from polishing filter (secondary filtration)	0	0	0	0	0
24	Filtered brine from polishing filter (secondary filtration)	0	0	0	0.0003201290	0
25	Filtered brine to brine filter backwash	0	0	0	0.0003201290	0
26	Filtered brine from polishing filter to ion-exchange	0	0	0	0.0003201290	0
27	Hold-up of filtered brine to ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0.0003201290	0
28	Filtered brine to ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0	0	0.0003201290	0
29	Demineralised water to ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0	0
30	Effluent from ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0.0000737956	0

cont.

Table A.2. *cont.*

| No | Stream Description | Mass Fraction | | | | | |
		H₂	O₂	HCl	NaOH	CaCO₃
31	Hold-up from ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0	0
32	Demineralised water to ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0	0
33	Effluent from ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0	0
34	Hold-up from ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0	0
35	Demineralised water to hydrochloric acid dilution - ion-exchange regeneration	0	0	0	0	0
36	Hydrochloric acid (31% m/m HCl) to hydrochloric acid dilution - ion-exchange regeneration	0	0	0.3148105150	0	0
37	Dilute hydrochloric acid to ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0.0700000000	0	0
38	Effluent from ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0.0301414020	0	0
39	Ca and Mg ions from ion-exchange to ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0	0
40	Hold-up from ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0.07	0	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		H₂	O₂	HCl	NaOH	CaCO₃
41	Hydrogen cation transfer from Acid Regeneration stage (IXR3) to Caustic Regeneration stage (IXR5)	0	0	0	0	0
42	Demineralised water to ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0	0
43	Hold-up from ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0	0
44	Effluent from ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0.0143505170	0	0
45	Demineralised water to caustic soda dilution - ion-exchange regeneration	0	0	0	0	0
46	Caustic soda (32% m/m NaOH) to caustic soda dilution - ion-exchange regeneration	0	0	0	0.3155743500	0
47	Dilute caustic soda to ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0	0	0.0400000000	0
48	Sodium cation transfer from Caustic Regeneration stage to ion-exchange	0	0	0	0	0
49	Effluent from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0	0	0.0205091790	0
50	Hold-up from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0	0	0.0400000000	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		H_2	O_2	HCl	NaOH	CaCO$_3$
51	Demineralised water to ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0	0
52	Effluent from ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0.0082442750	0
53	Hold-up from ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0	0
54	Effluent from ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0	0	0.0001288980	0
55	Hold-up from ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0	0	0.0003201290	0
56	Brine to ion-exchange	0	0	0	0.0003201290	0
57	Ultrapure brine to electrolyser	0	0	0	0.0003201280	0
58	Demineralised water to caustic soda dilution - electrolyser	0	0	0	0	0
59	Dilute caustic soda to electrolyser	0	0	0	0.2953790000	0
60	Caustic soda (32% m/m NaOH) from electrolyser	0	0	0	0.3155743500	0
61	Caustic soda (32% m/m NaOH) from electrolyser for internal use	0	0	0	0.3155743500	0
62	Caustic soda (32% m/m NaOH) to caustic evaporation	0	0	0	0.3155743500	0
63	Caustic soda (32% m/m NaOH) to caustic soda dilution - electrolyser	0	0	0	0.3155743500	0
64	Caustic soda (50% m/m NaOH) from caustic evaporation	0	0	0	0.5000000000	0
65	Wet hydrogen gas from electrolyser to hydrogen cooler	0.1019464240	0.0014696050	0	0	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		H₂	O₂	HCl	NaOH	CaCO₃
66	Wet chlorine gas from electrolyser to chlorine cooler	0.0000114902	0.0054736900	0	0	0
67	Lean brine from electrolyser	0	0	0	0	0
68	Hydrochloric acid (31% m/m HCl) to primary dechlorination	0	0	0.3148105150	0	0
69	Chlorinated condensate from chlorine cooler	0	0	0	0	0
70	Lean brine to primary dechlorination	0	0	0.0000990450	0	0
71	Waste gas to sodium hypochlorite synthesis	0	0	0	0	0
72	Lean brine to secondary dechlorination	0	0	0.0000994898	0	0
73	Demineralised water to caustic soda dilution - secondary dechlorination	0	0	0	0	0
74	Caustic soda (32% m/m NaOH) to caustic soda dilution - secondary dechlorination	0	0	0	0.3155743500	0
75	Dilute caustic soda to secondary dechlorination	0	0	0	0.1800000000	0
76	Demineralised water to sodium bisulphite dilution	0	0	0	0	0
77	Sodium bisulphite powder to sodium bisulphite dilution	0	0	0	0	0
78	Dilute sodium bisulphite to secondary dechlorination	0	0	0	0	0
79	Dilute sodium bisulphite and dilute caustic soda to secondary dechlorination	0	0	0	0.1004218190	0
80	Lean brine from secondary dechlorination	0	0	0	0.0003414670	0
81	Lean brine purge	0	0	0	0.0003414670	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		H_2	O_2	HCl	NaOH	$CaCO_3$
82	Lean brine to water make-up	0	0	0	0.0003414670	0
83	Demineralised water to water make-up	0	0	0		0
84	Condensate from caustic evaporation	0	0	0		0
85	Steam condensate from caustic evaporation	0	0	0		0
86	Ca and Mg load correction for condensate from caustic evaporation	0	0	0		0
87	Condensate to water make-up	0	0	0		0
88	Condensate from hydrogen cooler to drain	0	0	0		0
89	Hydrogen gas from hydrogen cooler	0.6942080120	0.0100073300	0		0
90	Hydrogen gas for Internal use	0.6942080120	0.0100073300	0		0
91	Hydrogen gas to hydrogen chiller	0.6942080120	0.0100073300	0		0
92	Condensate from hydrogen chiller to drain	0	0	0		0
93	Dry hydrogen gas to Alliance Peroxide	0.9164023990	0.0132103650	0		0
94	Lean brine to Resaturator - residual $NaHSO_3$ present	0	0	0	0.0002918660	0
95	Chlorine gas from chlorine cooler	0.0000142193	0.0067737830	0		0
96	Water removed from chlorine gas by sulphuric acid drying	0	0	0		0
97	Dry chlorine gas	0.0000144241	0.0068713710	0		0

cont.

Table A.2. *cont.*

		Mass Fraction				
No	Stream Description	INSOLS	Na$^+$	H$^+$	Mg^{2+}	Ca^{2+}
1	Oxygen for destruction of residual NaHSO$_3$ in lean brine	0	0	0	0	0
2	Lean brine to resaturator - NaHSO$_3$ destroyed	0	0	0	0	0
3	Raw salt to resaturator	0.0000983502	0	0	0	0
4	Brine to calcium precipitation	0.0000106937	0	0	0	0
5	Demineralised water to sodium carbonate dilution	0	0	0	0	0
6	Solid sodium carbonate to sodium carbonate dilution	0	0	0	0	0
7	Dilute sodium carbonate to calcium precipitation	0	0	0	0	0
8	Brine from calcium precipitation	0.0000106421	0	0	0	0
9	Brine from brine filter backwash	0.0001138630	0	0	0	0
10	Brine to magnesium precipitation	0.0000179222	0	0	0	0
11	Demineralised water to caustic soda dilution - magnesium precipitation	0	0	0	0	0
12	Caustic soda (32% m/m NaOH) to caustic soda dilution - magnesium precipitation	0	0	0	0	0
13	Dilute caustic soda to magnesium precipitation	0	0	0	0	0
14	Brine from magnesium precipitation	0.00000179057	0	0	0	0
15	Flocculant addition to brine	0	0	0	0	0
16	Brine to clarification	0.0000178219	0	0	0	0
17	Brine sludge	0.0043917850	0	0	0	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		INSOLS	Na$^+$	H$^+$	Mg^{2+}	Ca^{2+}
18	Brine to brine filter (primary filtration)	0.0000100000	0	0	0	0
19	Removed material from brine filter (primary filtration)	0.3263895410	0	0	0	0
20	Filtered brine from brine filter (primary filtration)	0.0000020000	0	0	0	0
21	Alpha-cellulose addition to filtered brine	0	0	0	0	0
22	Filtered brine to polishing filter (secondary filtration)	0.0000019952	0	0	0	0
23	Removed material from polishing filter (secondary filtration)	0.3249407890	0	0	0	0
24	Filtered brine from polishing filter (secondary filtration)	0	0	0	0	0
25	Filtered brine to brine filter backwash	0	0	0	0	0
26	Filtered brine from polishing filter to ion-exchange	0	0	0	0	0
27	Hold-up of filtered brine to ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0	0
28	Filtered brine to ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0	0	0	0
29	Demineralised water to ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0	0
30	Effluent from ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0	0

Table A.2. *cont.*

		Mass Fraction				
No	Stream Description	INSOLS	Na$^+$	H$^+$	Mg^{2+}	Ca^{2+}
31	Hold-up from ion-exchange regeneration - Brine Displacement stage (IXR1)	0	0	0	0	0
32	Demineralised water to ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0	0
33	Effluent from ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0	0
34	Hold-up from ion-exchange regeneration - Backwash stage (IXR2)	0	0	0	0	0
35	Demineralised water to hydrochloric acid dilution - ion-exchange regeneration	0	0	0	0	0
36	Hydrochloric acid (31% m/m HCl) to hydrochloric acid dilution - ion-exchange regeneration	0	0	0	0	0
37	Dilute hydrochloric acid to ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0	0
38	Effluent from ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0	0
39	Ca and Mg ions from ion-exchange to ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0.0458472880	0.9541527120
40	Hold-up from ion-exchange regeneration - Acid Regeneration stage (IXR3)	0	0	0	0	0

Table A.2. *cont.*

		Mass Fraction			
No Stream Description	INSOLS	Na$^+$	H$^+$	Mg^{2+}	Ca^{2+}
41 Hydrogen cation transfer from Acid Regeneration stage (IXR3) to Caustic Regeneration stage (IXR5)	0	0	1	0	0
42 Demineralised water to ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0	0
43 Hold-up from ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0	0
44 Effluent from ion-exchange regeneration - Acid Rinse stage (IXR4)	0	0	0	0	0
45 Demineralised water to caustic soda dilution - ion-exchange regeneration	0	0	0	0	0
46 Caustic soda (32% m/m NaOH) to caustic soda dilution - ion-exchange regeneration	0	0	0	0	0
47 Dilute caustic soda to ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0	0	0	0
48 Sodium cation transfer from Caustic Regeneration stage to ion-exchange	0	1	0	0	0
49 Effluent from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0	0	0	0
50 Hold-up from ion-exchange regeneration - Caustic Regeneration stage (IXR5)	0	0	0	0	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		INSOLS	Na⁺	H⁺	Mg²⁺	Ca²⁺
51	Demineralised water to ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0	0
52	Effluent from ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0	0
53	Hold-up from ion-exchange regeneration - Caustic Rinse stage (IXR6)	0	0	0	0	0
54	Effluent from ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0	0	0	0
55	Hold-up from ion-exchange regeneration - Brine Replacement stage (IXR7)	0	0	0	0	0
56	Brine to ion-exchange	0	0	0	0	0
57	Ultrapure brine to electrolyser	0	0	0	0	0
58	Demineralised water to caustic soda dilution - electrolyser	0	0	0	0	0
59	Dilute caustic soda to electrolyser	0	0	0	0	0
60	Caustic soda (32% m/m NaOH) from electrolyser	0	0	0	0	0
61	Caustic soda (32% m/m NaOH) from electrolyser for internal use	0	0	0	0	0
62	Caustic soda (32% m/m NaOH) to caustic evaporation	0	0	0	0	0
63	Caustic soda (32% m/m NaOH) to caustic soda dilution - electrolyser	0	0	0	0	0
64	Caustic soda (50% m/m NaOH) from caustic evaporation	0	0	0	0	0
65	Wet hydrogen gas from electrolyser to hydrogen cooler	0	0	0	0	0

cont.

Table A.2. *cont.*

No Stream Description	Mass Fraction				
	INSOLS	Na$^+$	H$^+$	Mg^{2+}	Ca^{2+}
66 Wet chlorine gas from electrolyser to chlorine cooler	0	0	0	0	0
67 Lean brine from electrolyser	0	0	0	0	0
68 Hydrochloric acid (31% m/m HCl) to primary dechlorination	0	0	0	0	0
69 Chlorinated condensate from chlorine cooler	0	0	0	0	0
70 Lean brine to primary dechlorination	0	0	0	0	0
71 Waste gas to sodium hypochlorite synthesis	0	0	0	0	0
72 Lean brine to secondary dechlorination	0	0	0	0	0
73 Demineralised water to caustic soda dilution - secondary dechlorination	0	0	0	0	0
74 Caustic soda (32% m/m NaOH) to caustic soda dilution - secondary dechlorination	0	0	0	0	0
75 Dilute caustic soda to secondary dechlorination	0	0	0	0	0
76 Demineralised water to sodium bisulphite dilution	0	0	0	0	0
77 Sodium bisulphite powder to sodium bisulphite dilution	0	0	0	0	0
78 Dilute sodium bisulphite to secondary dechlorination	0	0	0	0	0
79 Dilute sodium bisulphite and dilute caustic soda to secondary dechlorination	0	0	0	0	0
80 Lean brine from secondary dechlorination	0	0	0	0	0
81 Lean brine purge	0	0	0	0	0

cont.

Table A.2. *cont.*

No	Stream Description	Mass Fraction				
		INSOLS	Na⁺	H⁺	Mg²⁺	Ca²⁺
82	Lean brine to water make-up	0	0	0	0	0
83	Demineralised water to water make-up	0	0	0	0	0
84	Condensate from caustic evaporation	0	0	0	0	0
85	Steam condensate from caustic evaporation	0	0	0	0	0
86	Ca and Mg load correction for condensate from caustic evaporation	0	0	0	0	0
87	Condensate to water make-up	0	0	0	0	0
88	Condensate from hydrogen cooler to drain	0	0	0	0	0
89	Hydrogen gas from hydrogen cooler	0	0	0	0	0
90	Hydrogen gas for Internal use	0	0	0	0	0
91	Hydrogen gas to hydrogen chiller	0	0	0	0	0
92	Condensate from hydrogen chiller to drain	0	0	0	0	0
93	Dry hydrogen gas to Alliance Peroxide	0	0	0	0	0
94	Lean brine to Resaturator - residual NaHSO₃ present	0	0	0	0	0
95	Chlorine gas from chlorine cooler	0	0	0	0	0
96	Water removed from chlorine gas by sulphuric acid drying	0	0	0	0	0
97	Dry chlorine gas	0	0	0	0	0

A.3 THE HYDROCHLORIC ACID SYNTHESIS PLANT

Figure A.3 shows a block diagram of the hydrochloric acid synthesis plant. The hydrochloric acid synthesis unit and the hydrogen chloride gas scrubber are shown. Table A.3 presents the reconciled mass-balance for the hydrochloric acid synthesis plant.
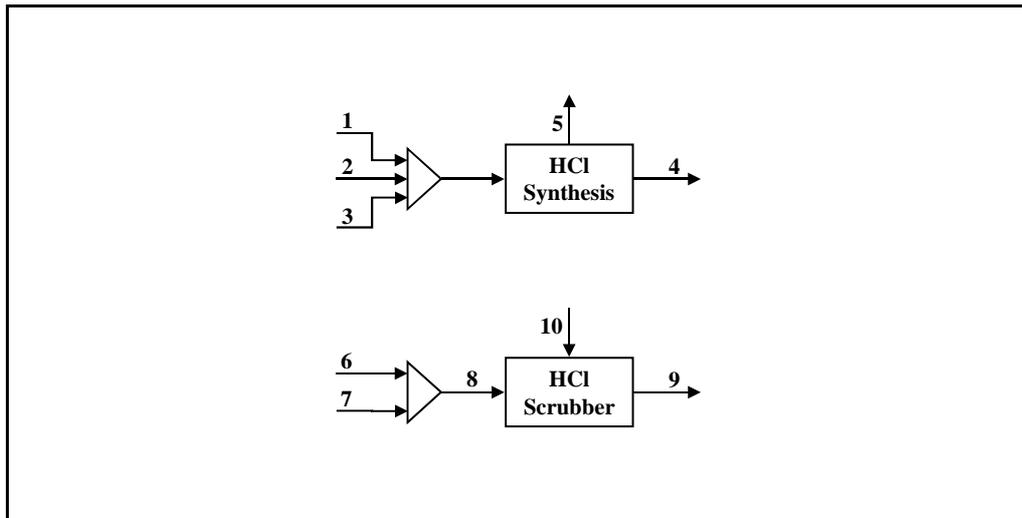
Figure A.3. *Block diagram of the hydrochloric acid synthesis plant showing the hydrochloric acid synthesis unit and the hydrogen chloride gas scrubber.*

A.4 THE SODIUM HYPOCHLORITE SYNTHESIS PLANT

Figure A.4 shows a block diagram of the sodium hypochlorite plant. Table A.4 presents the reconciled mass-balance of the plant.
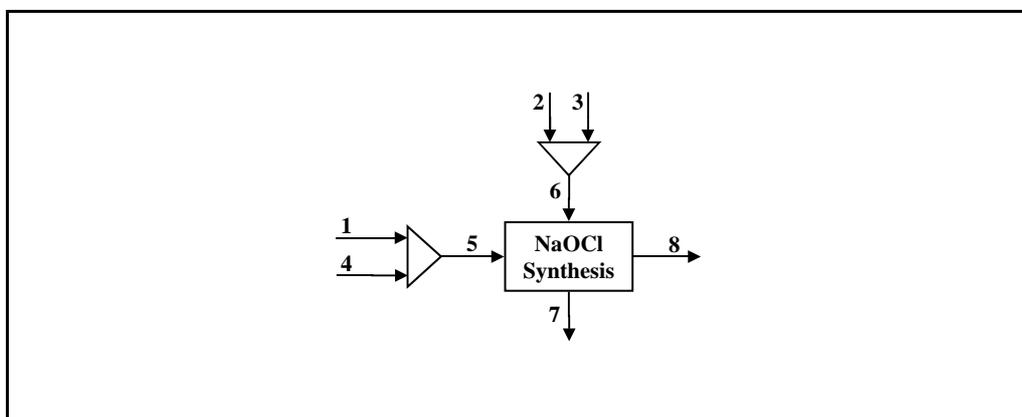
Figure A.4. *Block diagram of the sodium hypochlorite synthesis plant.*

Table A.3. *Reconciled mass-balance for the hydrochloric acid synthesis plant.*

No	Stream Description	Flow [kg/h]	Mass Fraction					
			MgCl$_2$	Na$_2$CO$_3$	Na$_2$SO$_4$	NaClO$_3$	NaCl	CaCl$_2$
1	Hydrogen gas to hydrochloric acid synthesis	30.1392	0	0	0	0	0	0
2	Chlorine gas to hydrochloric acid synthesis	752.1401	0	0	0	0	0	0
3	Demineralised water to hydrochloric acid synthesis	1628.6108	0.0000000078	0	0	0	0	0.0000000249
4	Hydrochloric acid (31 % m/m HCl)	2405.4937	0.0000000053	0	0	0	0	0.0000000169
5	Gases not absorbed in hydrochloric acid synthesis	5.3964	0	0	0	0	0	0
6	Caustic soda (32% m/m NaOH) to caustic soda dilution - hydrogen chloride scrubber	4.8110	0.0000000004	0.0034139200	0.0011060000	0.0000151000	0.0000539000	0.0000000014
7	Demineralised water to caustic soda dilution - hydrogen chloride scrubber	8.5882	0.0000000078	0	0	0	0	0.0000000249
8	Dilute caustic soda to hydrogen chloride scrubber	13.3992	0.0000000052	0.0012257710	0.0003971100	0.0000054200	0.0000194000	0.0000000165
9	Effluent from hydrogen chloride scrubber	14.4646	0.0000000048	0.0011354870	0.0003678610	0.0000050200	0.1180796300	0.0000000153
10	Hydrogen chloride mass-load to hydrogen chloride scrubber	1.0654	0	0	0	0	0	0

cont.

Table A.3. *cont.*

No	Stream Description	Mass Fraction					
		Cl_2	H_2O	H_2	O_2	HCl	NaOH
1	Hydrogen gas to hydrochloric acid synthesis	0	0.2957846580	0.6942080120	0.0100073300	0	0
2	Chlorine gas to hydrochloric acid synthesis	0.9790098060	0.0142021920	0.0000142000	0.0067737830	0	0
3	Demineralised water to hydrochloric acid synthesis	0	0.9999999670	0	0	0	0
4	Hydrochloric acid (31 % m/m HCl)	0.0000047300	0.6851847370	0	0	0.3148105150	0
5	Gases not absorbed in hydrochloric acid synthesis	0	0	0	1	0	0
6	Caustic soda (32% m/m NaOH) to caustic soda dilution - hydrogen chloride scrubber	0	0.6798367300	0	0	0	0.3155743500
7	Demineralised water to caustic soda dilution - hydrogen chloride scrubber	0	0.9999999670	0	0	0	0
8	Dilute caustic soda to hydrogen chloride scrubber	0	0.8850450440	0	0	0	0.1133072790
9	Effluent from hydrogen chloride scrubber	0	0.8562508230	0	0	0	0.0241611580
10	Hydrogen chloride mass-load to hydrogen chloride scrubber	0	0	0	0	1	0

Table A.4. *Reconciled mass-balance for the sodium hypochlorite synthesis plant.*

No	Stream Description	Flow [kg/h]	Mass Fraction					
			$MgCl_2$	Na_2CO_3	Na_2SO_4	$NaClO_3$	NaOCl	NaCl
1	Caustic soda (32% m/m NaOH) to sodium hypochlorite synthesis	2621.9384	0.0000000004	0.0034139200	0.0011060000	0.0000151000	0	0.0000539000
2	Chlorine vent from primary dechlorination to sodium hypochlorite synthesis	102.5690	0	0	0	0	0	0
3	Make-up chlorine to sodium hypochlorite synthesis	613.8537	0	0	0	0	0	0
4	Demineralised water to sodium hypochlorite synthesis	1139.0457	0.0000000078	0	0	0	0	0
5	Dilute caustic soda to sodium hypochlorite synthesis	3760.9841	0.0000000027	0.002379986	0.000771039	0.0000105000	0	0.0000376000
6	Total chlorine to sodium hypochlorite synthesis	716.4227	0	0	0	0	0	0
7	Water loss due to evaporation on sodium hypochlorite synthesis	341.5567	0	0	0	0	0	0
8	Sodium hypochlorite from sodium hypochlorite synthesis	4135.8501	0.0000000024	0.0021642680	0.0007011530	0.0017256740	0.1771898900	0.1438518930

cont.

Table A.4. *cont.*

		Mass Fraction					
No	Stream Description	CaCl₂	Cl₂	H₂O	H₂	O₂	NaOH
1	Caustic soda (32% m/m NaOH) to sodium hypochlorite synthesis	0.0000000014	0	0.6798367300	0	0	0.3155743500
2	Chlorine vent from primary dechlorination to sodium hypochlorite synthesis	0	1	0	0	0	0
3	Make-up chlorine to sodium hypochlorite synthesis	0	0.9931142050	0	0.0000144000	0.0068713710	0
4	Demineralised water to sodium hypochlorite synthesis	0.00000000249	0	0.9999999670	0	0	0
5	Dilute caustic soda to sodium hypochlorite synthesis	0.0000000085	0	0.7768008630	0	0	0.2200000000
6	Total chlorine to sodium hypochlorite synthesis	0	0.9941000320	0	0.0000124000	0.0058876090	0
7	Water loss due to evaporation on sodium hypochlorite synthesis	0	0	0.9876246870	0.0000259000	0.0123493890	0
8	Sodium hypochlorite from sodium hypochlorite synthesis	0.0000000078	0	0.6685833740	0	0	0.0057837380

A.5 THE HYDECAT DESTRUCTION PLANT

Figure A.5 shows a block diagram of the Hydecat destruction plant. The reconciled mass-balance for this plant is presented in Table A.5.
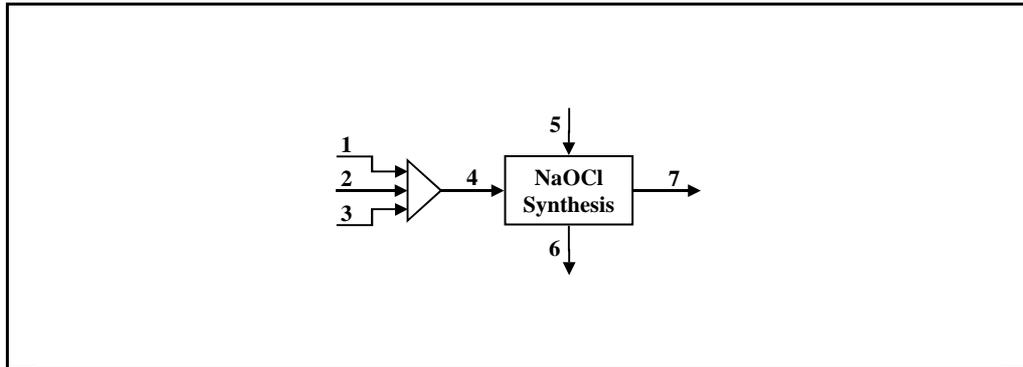
Figure A.5. *Block diagram of the Hydecat destruction plant.*

A.6 THE CAUSTIC EVAPORATORS

Figure A.6 shows a block diagram of the caustic evaporators. The reconciled mass-balance for this plant is presented in Table A.6.
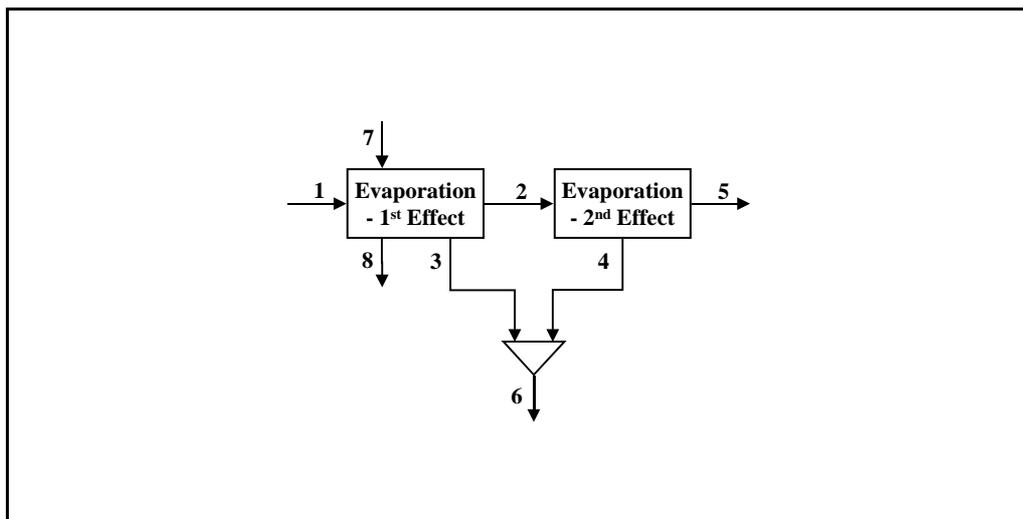
Figure A.6. *Block diagram of the caustic evaporators.*

Table A.5. *Reconciled mass-balance for the Hydecat destruction plant.*

No	Stream Description	Flow [kg/h]	MgCl₂	Na₂CO₃	Na₂SO₄	NaClO₃	NaOCl	NaCl
1	Steam injection to Hydecat destruction plant	220.0000	0	0	0	0	0	0
2	Waste sodium hypochlorite to Hydecat destruction plant	484.6839	0.0000000024	0.0021642680	0.0007011530	0.0017256740	0.1771898900	0.1438518930
3	Umbogintwini River water to waste sodium hypochlorite dilution	1442.3433	0.0000274228	0.0000145736	0.0000606386	0.0000000000	0.0000000000	0.0000694903
4	Dilute sodium hypochlorite to Hydecat destruction plant	2147.0273	0.0000184228	0.0004983660	0.0001990190	0.0003895650	0.0400000000	0.0325207460
5	Nickel loading on Hydecat destruction plant	0.0064	0	0	0	0	0	0
6	Waste gas from Hydecat destruction plant	18.4417	0	0	0	0	0	0
7	Hydecat destruction plant effluent	2128.5920	0.0000185824	0.0005026830	0.0002007430	0.0003929390	0.0000365088	0.0644485310

cont.

Table A.5. *cont.*

| | | | | Mass Fraction | | | | |
No	Stream Description	CaCl₂	Cl₂	H₂O	O₂	NaOH	Ni²⁺	INSOLS
1	Steam injection to Hydecat destruction plant	0	0	1	0	0	0	0
2	Waste sodium hypochlorite to Hydecat destruction plant	0	0	0.668583374	0	0.005783738	0	0
3	Umbogintwini water to waste sodium hypochlorite dilution	0	0	0.999762227	0	0	0	0.0000241061
4	Dilute sodium hypochlorite to Hydecat destruction plant	0	0	0.925024119	0	0.001305659	0	0.0000161941
5	Nickel loading on Hydecat destruction plant	0	0	0	0	0	1	0
6	Waste gas from Hydecat destruction plant	0	0	0	1	0	0	0
7	Hydecat destruction plant effluent	0	0	0.933035562	0	0.001316967	0.0000029996	0.0000163344

Table A.6. *Reconciled mass-balance for the caustic evaporators.*

No	Stream Description	Flow [kg/h]	Mass Fraction			
			$MgCl_2$	Na_2CO_3	Na_2SO_4	$NaClO_3$
1	Caustic soda (32 % m/m NaOH) to caustic evaporation	8879.6990	0.0000000004	0.0034139200	0.0011060000	0.0000150959
2	Caustic soda (38 % m/m NaOH) from primary effect	7374.2243	0.0000000005	0.0041108840	0.0013317940	0.0000181778
3	Condensate from primary effect of caustic evaporation	1505.4747	0	0	0	0
4	Condensate from secondary effect of caustic evaporation	1769.8138	0	0	0	0
5	Caustic soda (50 % m/m NaOH) from caustic evaporation	5604.4105	0.0000000007	0.0054090580	0.0017523600	0.0000239181
6	Total process condensate from caustic evaporation	3275.2885	0	0	0	0
7	Steam to caustic evaporation	2729.9352	0.0000000078	0	0	0
8	Steam condensate from caustic evaporation	2729.9352	0.0000000078	0	0	0

cont.

Table A.6. *cont.*

No	Stream Description	Mass Fraction			
		NaCl	$CaCl_2$	H_2O	NaOH
1	Caustic soda (32 % m/m NaOH) to caustic evaporation	0.0000539022	0.0000000014	0.6798367300	0.3155743500
2	Caustic soda (38 % m/m NaOH) from primary effect	0.0000649066	0.0000000017	0.6144742350	0.3800000000
3	Condensate from primary effect of caustic evaporation	0.0000000000	0.0000000000	1.0000000000	0.0000000000
4	Condensate from secondary effect of caustic evaporation	0	0	1	0
5	Caustic soda (50 % m/m NaOH) from caustic evaporation	0.0000854034	0.0000000023	0.49272926	0.5
6	Total process condensate from caustic evaporation	0.0000000000	0.0000000000	1.0000000000	0.0000000000
7	Steam to caustic evaporation	0.0000000000	0.0000000249	0.9999999670	0.0000000000
8	Steam condensate from caustic evaporation	0.0000000000	0.0000000249	0.9999999670	0.0000000000

A.7 THE COOLING CIRCUITS

Figure A.7 shows a block diagram of the four cooling circuits located on the chlor-alkali complex. The reconciled mass-balance for the cooling circuits are presented in Table A.7.
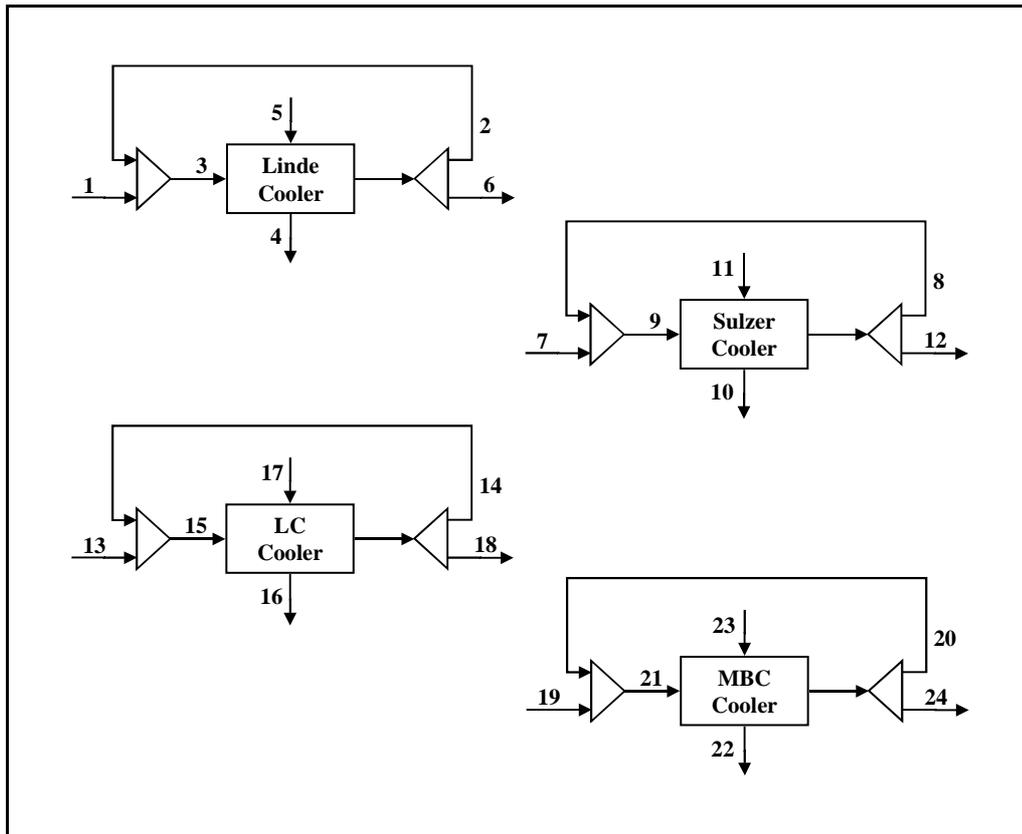
Figure A.7. *Block diagram of the four cooling circuits located on the chlor-alkali complex.*

Table A.7. *Reconciled mass-balance for the four cooling circuits on the chlor-alkali complex.*

No	Stream Description	Flow [kg/h]	Mass Fraction				
			MgCl$_2$	Na$_2$CO$_3$	Na$_2$SO$_4$	NaCl	
1	Make-up water to Linde cooling tower	3325.3040	0.0000274228	0.0000145736	0.0000606386	0.0000694903	
2	Recycled water from cooling circuit to Linde cooling tower	96234.6960	0.0001382470	0.0001395890	0.0003056990	0.0003503240	
3	Total water to Linde cooling tower	99560.0000	0.0001345460	0.0001354130	0.0002975140	0.0003409440	
4	Evaporation from Linde cooling tower	2665.7394	0	0	0	0	
5	Na$_2$CO$_3$ loading to Linde cooling tower	0.0436	0	1	0	0	
6	Blowdown from Linde cooling tower	659.6083	0.0001382470	0.0001395890	0.0003056990	0.0003503240	
7	Make-up water to Sulzer cooling tower	1055.3360	0.0000274228	0.0000145736	0.0000606386	0.0000694903	
8	Recycled water from cooling circuit to Sulzer cooling tower	98504.6640	0.0000446165	0.0000471761	0.0000986582	0.0001130600	
9	Total water to Sulzer cooling tower	99560.0000	0.0000444343	0.0000468306	0.0000982552	0.0001125980	
10	Evaporation from Sulzer cooling tower	406.7071	0	0	0	0	
11	Na$_2$CO$_3$ loading to Sulzer cooling tower	0.0152	0	1	0	0	
12	Blowdown from Sulzer cooling tower	648.6441	0.0000446165	0.0000471761	0.0000986582	0.0001130600	

cont.

Table A.7. *cont.*

No	Stream Description	Flow [kg/h]	Mass Fraction				
			MgCl₂	Na₂CO₃	Na₂SO₄	NaCl	
13	Make-up water to LC cooling tower	18548.0280	0.0000274228	0.0000145736	0.0000606386	0.0000694903	
14	Recycled water from cooling circuit to LC cooling tower	877491.9720	0.0002102210	0.0002067860	0.0004648520	0.0005327080	
15	Total water to LC cooling tower	896040.0000	0.0002064370	0.0002028080	0.0004564840	0.0005231200	
16	Evaporation from LC cooling tower	16128.7200	0	0	0	0	
17	Na₂CO₃ loading to LC cooling tower	0.2300	0	1	0	0	
18	Blowdown from LC cooling tower	2419.5380	0.0002102210	0.0002067860	0.0004648520	0.0005327080	
19	Make-up water to MBC cooling tower	12347.0330	0.0000274228	0.0000145736	0.0000606386	0.0000694903	
20	Recycled water from cooling circuit to MBC cooling tower	810018.5670	0.0002102210	0.0002067860	0.0004648520	0.0005327080	
21	Total water to MBC cooling tower	823365.6000	0.0002074770	0.0002039010	0.0004587830	0.0005257540	
22	Evaporation from MBC cooling tower	10736.5504	0	0	0	0	
23	Na₂CO₃ loading to MBC cooling tower	0.1531	0	1	0	0	
24	Blowdown from MBC cooling tower	1610.6357	0.0002102210	0.0002067860	0.0004648520	0.0005327080	

cont.

Table A.7. *cont.*

		Mass Fraction			
No	Stream Description	CaCl$_2$	H$_2$O	INSOLS	TDS
1	Make-up water to Linde cooling tower	0.0000415421	0.9997622270	0.0000241061	0.0002136670
2	Recycled water from cooling circuit to Linde cooling tower	0.0002094270	0.9987351870	0.0001215270	0.0011432860
3	Total water to Linde cooling tower	0.0002038200	0.9987694900	0.0001182730	0.0011122370
4	Evaporation from Linde cooling tower	0	1	0	0
5	Na$_2$CO$_3$ loading to Linde cooling tower	0	0	0	1
6	Blowdown from Linde cooling tower	0.0002094270	0.9987351870	0.0001215270	0.0011432860
7	Make-up water to Sulzer cooling tower	0.0000415421	0.9997622270	0.0000241061	0.0002136670
8	Recycled water from cooling circuit to Sulzer cooling tower	0.0000675884	0.9995896810	0.0000392203	0.0003710990
9	Total water to Sulzer cooling tower	0.0000673123	0.9995915090	0.0000390601	0.0003694300
10	Evaporation from Sulzer cooling tower	0	1	0	0
11	Na$_2$CO$_3$ loading to Sulzer cooling tower	0	0	0	1
12	Blowdown from Sulzer cooling tower	0.0000675884	0.9995896810	0.0000392203	0.0003710990

cont.

Table A.7. *cont.*

No	Stream Description	Mass Fraction			
		CaCl$_2$	H$_2$O	INSOLS	TDS
13	Make-up water to LC cooling tower	0.0000415421	0.9997622270	0.0000241061	0.0002136670
14	Recycled water from cooling circuit to LC cooling tower	0.0003184590	0.9980821780	0.0001847960	0.0017330270
15	Total water to LC cooling tower	0.0003127270	0.9981169550	0.0001814690	0.0017015760
16	Evaporation from LC cooling tower	0	1	0	0
17	Na$_2$CO$_3$ loading to LC cooling tower	0	0	0	1
18	Blowdown from LC cooling tower	0.0003184590	0.9980821780	0.0001847960	0.0017330270
19	Make-up water to MBC cooling tower	0.0000415421	0.9997622270	0.0000241061	0.0002136670
20	Recycled water from cooling circuit to MBC cooling tower	0.0003184590	0.9980821780	0.0001847960	0.0017330270
21	Total water to MBC cooling tower	0.0003143010	0.9981074020	0.0001823830	0.0017102150
22	Evaporation from MBC cooling tower	0	1	0	0
23	Na$_2$CO$_3$ loading to MBC cooling tower	0	0	0	1
24	Blowdown from MBC cooling tower	0.0003184590	0.9980821780	0.0001847960	0.0017330270

A.8 SUPPORT OPERATIONS, POINT SOURCES AND DEMANDS

Figure A.8 shows a block diagram of the various support operations, point sources and demands located on the chlor-alkali complex. Table A.8 presents the mass-balance for the pump seals; Table A.9 presents the mass-balance for the pressure testing operations; Table A.10 presents the mass-balance for the cylinder steaming operations; Table A.11 presents the mass-balance for the plant washdown operations; and, Table A.12 and Table A.13 present the flow and composition data for the point sources and demands respectively.
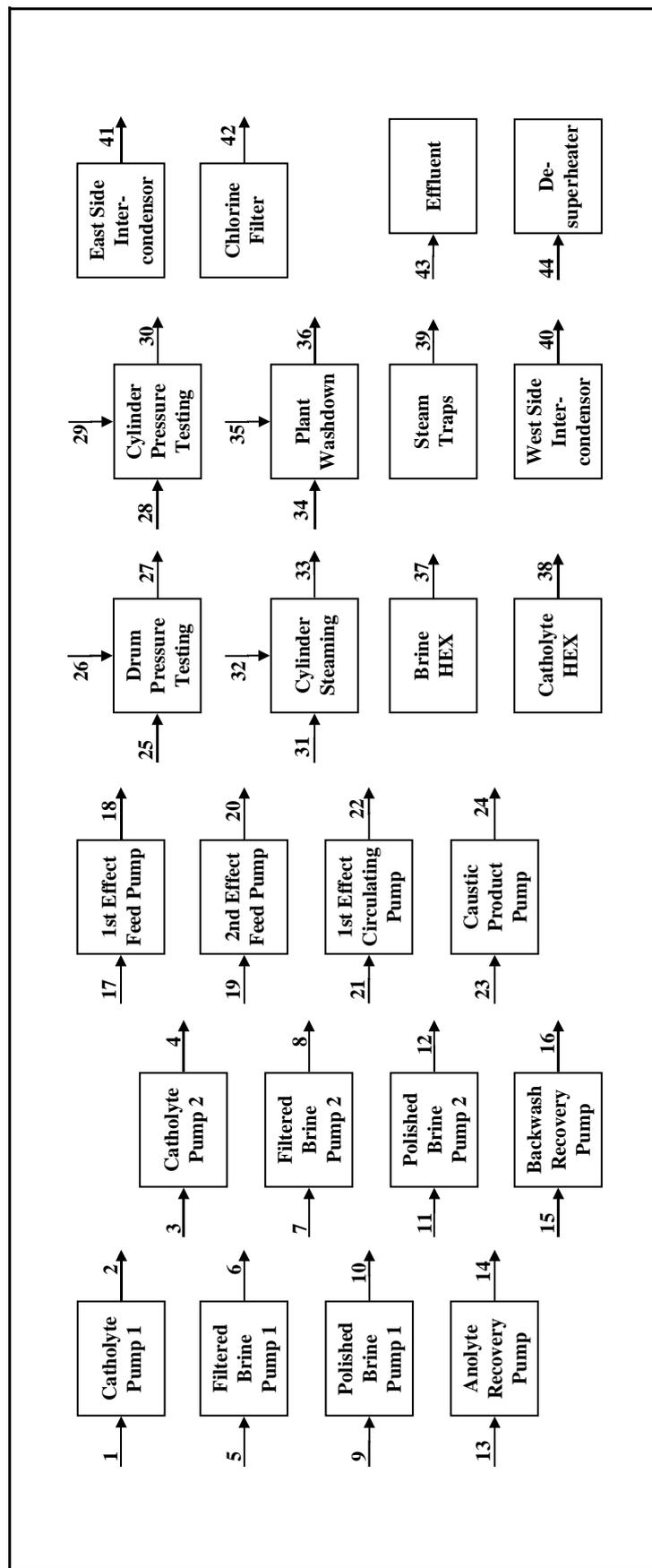
Figure A.8. *Block diagram of the support operations, point sources and demands located on the chlor-alkali complex.*

Table A.8. *Mass-balance for the distribution of pump seal water on the chlor-alkali complex.*

| No | Stream Description | Flow [kg/h] | Mass Fraction | | |
			MgCl₂	CaCl₂	H₂O
1	Pump seal water - catholyte pump 1	149.3400	0.0000000078	0.0000000249	0.9999999670
2	Pump seal water effluent - catholyte pump 1	149.3400	0.0000000078	0.0000000249	0.9999999670
3	Pump seal water - catholyte pump 2	149.3400	0.0000000078	0.0000000249	0.9999999670
4	Pump seal water effluent - catholyte pump 2	149.3400	0.0000000078	0.0000000249	0.9999999670
5	Pump seal water - filtered brine pump 1	149.3400	0.0000000078	0.0000000249	0.9999999670
6	Pump seal water effluent - filtered brine pump 1	149.3400	0.0000000078	0.0000000249	0.9999999670
7	Pump seal water - filtered brine pump 2	149.3400	0.0000000078	0.0000000249	0.9999999670
8	Pump seal water effluent - filtered brine pump 2	149.3400	0.0000000078	0.0000000249	0.9999999670
9	Pump seal water - polished brine pump 1	149.3400	0.0000000078	0.0000000249	0.9999999670
10	Pump seal water effluent - polished brine pump 1	149.3400	0.0000000078	0.0000000249	0.9999999670
11	Pump seal water - polished brine pump 2	149.3400	0.0000000078	0.0000000249	0.9999999670
12	Pump seal water effluent - polished brine pump 2	149.3400	0.0000000078	0.0000000249	0.9999999670

cont.

Table A.8. *cont.*

| No | Stream Description | Flow [kg/h] | Mass Fraction | | |
			MgCl₂	CaCl₂	H₂O
13	Pump seal water - anolyte recovery pump	149.3400	0.0000000078	0.0000000249	0.9999999670
14	Pump seal water effluent - anolyte recovery pump	149.3400	0.0000000078	0.0000000249	0.9999999670
15	Pump seal water - backwash recovery pump	149.3400	0.0000000078	0.0000000249	0.9999999670
16	Pump seal water effluent - backwash recovery pump	149.3400	0.0000000078	0.0000000249	0.9999999670
17	Pump seal water - 1st effect circulating pump	149.3400	0.0000000078	0.0000000249	0.9999999670
18	Pump seal water effluent - 1st effect circulating pump	149.3400	0.0000000078	0.0000000249	0.9999999670
19	Pump seal water - 2nd effect circulating pump	149.3400	0.0000000078	0.0000000249	0.9999999670
20	Pump seal water effluent - 2nd effect circulating pump	149.3400	0.0000000078	0.0000000249	0.9999999670
21	Pump seal water - 1st effect feed pump	149.3400	0.0000000078	0.0000000249	0.9999999670
22	Pump seal water effluent - 1st effect feed pump	149.3400	0.0000000078	0.0000000249	0.9999999670
23	Pump seal water - caustic product pump	149.3400	0.0000000078	0.0000000249	0.9999999670
24	Pump seal water effluent - caustic product pump	149.3400	0.0000000078	0.0000000249	0.9999999670

Table A.9. *Mass-balance for pressure testing operations occurring at the chlor-alkali complex (time-averaged values).*

			Mass Fraction			
No	Stream Description	Flow [kg/h]	$MgCl_2$	Na_2CO_3	Na_2SO_4	NaCl
25	Water to drum pressure testing	44.7877	0.0000274228	0.0000145736	0.0000606386	0.0000694903
26	Calculated loading on drum pressure testing	0.0124	0	0	0	0.9942056039
27	Effluent from drum pressure testing	44.8000	0.0000274152	0.0000145696	0.0000606218	0.0003440000
28	Water to cylinder pressure testing	19.9056	0.0000274228	0.0000145736	0.0000606386	0.0000694903
29	Calculated loading on cylinder pressure testing	0.0094	0	0	0	0.9974454079
30	Effluent from cylinder pressure testing	19.9150	0.0000274099	0.0000145668	0.0000606101	0.0005380000

cont.

Table A.9. *cont.*

		Mass Fraction			
No	Stream Description	$CaCl_2$	Cl_2	H_2O	INSOLS
25	Water to drum pressure testing	0.0000415421	0.0000000000	0.9997622266	0.0000241061
26	Calculated loading on drum pressure testing	0.0000000000	0.0057943961	0.0000000000	0.0000000000
27	Effluent from drum pressure testing	0.0000415306	0.0000016000	0.9994861634	0.0000240994
28	Water to cylinder pressure testing	0.0000415421	0.0000000000	0.9997622266	0.0000241061
29	Calculated loading on cylinder pressure testing	0.0000000000	0.0025545921	0.0000000000	0.0000000000
30	Effluent from cylinder pressure testing	0.0000415225	0.0000012000	0.9992925960	0.0000240947

Table A.10. *Mass-balance for the cylinder steaming operation occurring at the chlor-alkali complex (time-averaged values).*

No	Stream Description	Flow [kg/h]	Mass Fraction			
			$MgCl_2$	NaCl	$CaCl_2$	H_2O
31	Steam to cylinder steaming	4.7852	0.00000000078	0	0.0000000249	0.999999967
32	Calculated loading on cylinder steaming	0.0045	0	1	0	0
33	Effluent from cylinder steaming	4.7896	0.0000000078	0.0009340000	0.0000000249	0.999065967

Table A.11. *Mass-balance for the plant washdown operations occurring at the chlor-alkali complex (time-averaged values).*

No	Stream Description	Flow [kg/h]	Mass Fraction						
			$MgCl_2$	Na2CO3	Na_2SO_4	NaCl	$CaCl_2$	H_2O	INSOLS
34	Water to plant washdown	157.0866	0.0000274228	0.0000145736	0.0000606386	0.0000694903	0.0000415421	0.9997622266	0.0000241061
35	Calculated loading on plant washdown	3.2058	0	0	0	0	0	0	1
36	Plant washdown effluent	160.2925	0.0000268743	0.00001142822	0.0000594258	0.0000681005	0.0000407112	0.9797669820	0.0200236239

Table A.12. *Flow and composition data for point sources located on the chlor-alkali complex.*

No	Stream Description	Flow [kg/h]	Mass Fraction			
			$MgCl_2$	$CaCl_2$	Cl_2	H_2O
37	Brine heat-exchanger condensate	746.7000	0.0000000078	0.0000000249	0	0.9999999670
38	Catholyte heat-exchanger condensate	319.6523	0.0000000078	0.0000000249	0	0.9999999670
39	Condensate from steam traps	298.6800	0.0000000078	0.0000000249	0	0.9999999670
40	West side intercondensor condensate	81.4401	0.0000000078	0.0000000249	0	0.9999999670
41	East side intercondensor condensate	210.8681	0.0000000078	0.0000000249	0	0.9999999670
42	Effluent from chlorine filter	50.0553	0.0000000078	0.0000000248	0.0055000000	0.9944999670

Table A.13. *Flow and composition data for point demands located on the chlor-alkali complex.*

No	Stream Description	Flow [kg/h]	Mass Fraction			
			$MgCl_2$	Na_2CO_3	Na_2SO_4	$NaClO_3$
43	Caustic soda (32% m/m NaOH) to effluent	96.4535	0.0000000004	0.0034139200	0.0011060000	0.0000150959
44	Demineralised water to desuperheater	398.2400	0.0000000078	0	0	0

cont.

Table A.13. *cont.*

No	Stream Description	Mass Fraction			
		$NaCl$	$CaCl_2$	H_2O	$NaOH$
43	Caustic soda (32% m/m NaOH) to effluent	0.0000539022	0.0000000014	0.6798367297	0.3155743503
44	Demineralised water to desuperheater	0	0.0000000249	0.9999999672	0

B

WATER PINCH ANALYSIS

Appendix B provides details of the results which might be expected from applying current Water Pinch Analysis theory and tools to the problem presented by the chlor-alkali complex. Many of the issues associated with the application of this approach to the problem are presented elsewhere (Gianadda et al. 2000; 2002) and are considered here only briefly. It is noted however that the results presented in **Appendix B** supersede those presented in Gianadda et al (2000; 2002).

B.1 THE APPLICATION OF WATER PINCH ANALYSIS TO THE CHLOR-ALKALI COMPLEX

The Water Pinch Analysis software available for this project was the WaterPinch™ module of the Linnhoff March WaterTarget™ software suite (Linnhoff March Limited, 2001). As noted in **Chapter 4**, it is the capabilities of the optimisation tools and methods which strongly influence the way in which the problem is formulated. In this regard, current versions of the software do not consider the possibility that interactions exist between species. Species are further considered to be exclusively undesirable. It is therefore necessary to formulate the problem in such a way that these issues are circumvented. This however requires additional constraints, which further do not have physical justification, to be included in the model. The resource use strategies which are identified by this approach are consequently not as efficient as those that could be achieved when these constraints are absent, that is, using Combined Water and Materials Pinch Analysis.

As an illustration of the approach required in formulating the problem such that Water Pinch Analysis theory may be applied, a dilution operation is considered. In his study on the chlor-alkali complex, Gardner (1999) set the maximum concentration constraint on the reagent species entering the dilution operation as part of the dilution water equal to the reagent species concentration produced by the dilution operation. According to this concentration constraint it is possible for any water source to enter the dilution operation as dilution water provided that

its concentration is less than or equal to the reagent species concentration produced by the dilution operation. With this study being based on a single species, that is, the reagent species, this measure encouraged the recovery of the reagent-containing effluents. With the recovery of reagent-containing effluent to the dilution operation, a reduction in the amount of concentrated reagent required by the dilution operation was achieved. However, a greater quantity of dilution water was needed to meet the flowrate requirement of the dilution operation. An iterative procedure was thus used to solve the problem.

While this approach is successful when a single species is considered, it cannot be applied to the multiple species situation. According to the approach used by Gardner, species concentration limits on the dilution water entering the dilution operation are set at the level produced by that operation. In the present operating scenario, only concentrated reagent and demineralised water are used to produce the dilute reagent source. The mass-load of contaminants present in this dilute reagent source is thus at its theoretical minimum. In addition, the ratio of reagent species mass-load to contaminant species mass-load is at its theoretical maximum. This ratio may be used to assess whether the use of a particular reagent-containing effluent will be feasible. Effluent with a greater ratio of reagent species mass-load to contaminant species mass-load may be used for dilution without downstream penalty. Effluent for which the ratio of reagent species mass-load to contaminant species mass-load is lower than this theoretical maximum may be used for dilution, but there may be a downstream penalty involved in its use. This penalty takes the form of a cost associated with the added effort required to remove the additional mass-load of contaminant from the system.

The present version of WaterPinch^{TM} does not allow concentration equality or concentration minimum constraints. Although desirable, reagent species can thus only be represented in terms of the maximum concentration constraints. With the present version of WaterPinch^{TM} not being able to account for possible downstream penalties incurred through the reuse of reagent-containing effluent, it is necessary to formulate the concentration constraints for contaminant species in such a way that reagent-containing effluent is used only if it is certain that there will be no penalty incurred through its use. This implies that the ratio of the mass-load of reagent species to the mass-load of contaminant species must be maintained at the theoretical maximum. The concentration constraints at the inlet to the dilution operation as thus set as follows:

- For the reagent species, the concentration limit is set at the concentration produced by the dilution operation

- For the contaminant species, the concentration limits are set at the level of the dilution water currently entering the operation.

With this formulation, only the dilution water side of the operation is considered. While this set of constraints does guarantee that there is no downstream penalty incurred through the reuse of effluent, it is noted that there is no physical justification for these constraints.

The application of Water Pinch Analysis to the chlor-alkali complex follows the same decomposition procedure as outlined in **Chapter 5**. Similar assumptions as to the reuse of water from one subsystem to another are included. These subsystems are initially optimised in isolation from each other and are subsequently integrated. While details of the modelling are not presented here, it is noted that a significant element of the modelling is directed towards ensuring that there are no downstream penalties incurred through the reuse of water and reagent. Table B.1 presents a comparison between the existing network configuration and that proposed by Water Pinch Analysis for the various subsystems functioning on an integrated basis. Table B.2 presents these figures in terms of a total inventory of materials used and effluent produced by the complex.

Table B.1. *Comparison of materials used and waste generated by the chlor-alkali complex in its existing network configuration and the network configuration proposed by the application of Water Pinch Analysis. These figures reflect the performance of the different subsystems in combination with each other.*

	Unit	Existing Configuration	Water Pinch Configuration	Percentage Improvement [%]
Demineralisation Plant Subsystem				
Umbogintwini River Water	[t/y]	55 582	37 578	32
Umgeni Water	[t/y]	55 582	32 407	42
Total Water	[t/y]	111 165	69 985	37
Demineralised Water	[t/y]	104 308	68 497	34
Caustic Soda (32% m/m NaOH)	[t/y]	170	112	34
Hydrochloric Acid (31% m/m HCl)	[t/y]	153	100	34
Effluent	[t/y]	9 779	4 678	52
Annual Saving* (AS1)	[R/y]	-	205 024	-
Unit cost of Demineralised Water	[R/t]	4.710	4.363	7.4
Number of Regeneration Cycles	[/y]	436	286	34
Duration of Normal Cycle of Operation	[h]	16.6	27.0	-

cont.

Table B.1. *cont.*

	Unit	Existing Configuration	Water Pinch Configuration	Percentage Improvement [%]
Chemical Production Subsystem				
Demineralised Water	[t/y]	104 308	68 497	34
Umbogintwini River Water	[t/y]	14 378	14 378	0
Total Water	[t/y]	118 686	82 875	30
Raw Salt	[t/y]	51 464	51 464	0
Sodium Carbonate	[t/y]	380	380	0
Sodium Bisulphite	[t/y]	129.4	129.4	0
Caustic Soda (32% m/m NaOH)	[t/y]	24 196	24 196	0
Hydrochloric Acid (31% m/m HCl)	[t/y]	2 584	2 584	0
Chlorine	[t/y]	11 802	11 802	0
Hydrogen	[t/y]	260.4	260.4	0
Steam	[t/y]	25 487	25 487	0
Flocculant	[kg/y]	2 797	2 797	0
Alpha-Cellulose	[kg/y]	11 188	11 188	0
Effluent	[t/y]	86 655	52 891	39
Solid Waste	[kg/y]	14 349	14 349	0
Annual Saving* (AS2)	[R/y]	-	271 560	-
Cooling Circuit Subsystem				
Umbogintwini River Water	[t/y]	304 782	298 138	2.2
Effluent	[t/y]	46 124	39 474	14
Annual Saving* (AS3)	[R/y]	-	66 296	-
Total Annual Saving* (AS1 + AS2 + AS3)	[R/y]	-	542 881	-

* *These costs correspond to those for the year 2000.*

Table B.2. *Comparison of the total consumption of materials and waste generated across all subsystems of the chlor-alkali complex in its existing network configuration and the network configuration proposed by the application of Water Pinch Analysis. Only those items for which a change was observed are reported.*

	Unit	Existing Configuration	Water Pinch Configuration	Percentage Improvement [%]
Umbogintwini River Water	[t/y]	374 743	350 093	6.6
Umgeni Water	[t/y]	55 582	32 407	42
Total Water	[t/y]	430 325	382 500	11
Demineralised Water	[t/y]	104 308	68 497	34
Caustic Soda (32% m/m NaOH)	[t/y]	24 366	24 308	0.2
Hydrochloric Acid (31% m/m HCl)	[t/y]	2 737	2 684	1.9
Effluent	[t/y]	142 557	97 044	32
Annual Saving*	[R/y]	-	542 881	-

* *These costs correspond to those for the year 2000.*

Some comments on the figures presented in Table B.1 and Table B.2 are as follows:

- While material consumption figures are provided, these were derived by mass-balance from the proposed network configurations provided by WaterPinch™.

- Slight decreases in the use of caustic soda and hydrochloric acid are observed in the proposed network configuration. These decreases may be attributed to the smaller demand for demineralised water by the complex as a whole.

- With it not being possible to account for the effect of changing water quality at the inlet to the demineralisation plant, the concentration constraints on water quality were formulated according to an equal ratio blend of Umgeni Water and Umbogintwini River water. The recovery of good quality water from the chemical production subsystem results in the blend ratio changing such that more Umbogintwini River water, the less expensive but more contaminated source, is used. This blend however changes only within the limits of the concentration constraints on the water at the inlet to the demineralisation plant.

- It is possible to formulate the model for the cooling circuit subsystem in WaterPinch™ in the same way as it is formulated in GAMS for Combined Water and Materials Pinch Analysis. The solution provided by WaterPinch™ for this subsystem is identical in terms of water consumption and effluent production to that provided by GAMS. The sensitivity data provided by WaterPinch™ similarly identifies the concentration constraint for Na_2CO_3 at the

inlet to the LC cooling tower as the key sensitivity. That the results provided by the GAMS formulation of the model coincide with those provided by WaterPinch™ is considered a benchmark on the performance of the GAMS model.

- With the exception of the cooling circuit subsystem, the sensitivity data provided by WaterPinch™ for the other subsystems does not coincide with that provided by GAMS. This is due to the additional constraints included in the WaterPinch™ model. With some of these constraints not having physical justification, the insight into the performance of the system is not as useful as when these constraints are absent.

As a concluding comment to this appendix, these results prove that in the absence of more advanced approaches, it is still possible to identify substantial savings using standard approaches. Obviously, with the inclusion of the more restrictive constraints in the WaterPinch™ model, the resource use strategy will not be as efficient as could be achieved if these constraints were absent.

B.2 APPENDIX REFERENCES

GARDNER GA (1999) *Liquid waste management on a chloro-alkali complex.* MScEng Dissertation, Pollution Research Group, School of Chemical Engineering, University of Natal, Durban, South Africa.

GIANADDA P, BROUCKAERT CJ and BUCKLEY CA (2000) *The application of pinch analysis to water, reagent and effluent management in a chlor-alkali facility.* Proceedings of the 9th National Meeting of the South African Institute of Chemical Engineers, Secunda, South Africa.

GIANADDA P, BROUCKAERT CJ, SAYER R and BUCKLEY CA (2002) *The application of pinch analysis to water, reagent and effluent management in a chlor-alkali facility.* Water Sci & Technol **46** (9) 21-28.

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C

PROCESS MODULE MODELS

Appendix C presents the more detailed aspects of the modelling of the process modules associated with the chemical production subsystem and the cooling circuit subsystem. The material presented in this appendix is considered supplementary to that presented in **Chapter 5**. **Section C.1** presents the process modules associated with the chemical production subsystem while **Section C.2** presents the process modules associated with the cooling circuit subsystem. A concluding remark to this appendix is presented in **Section C.3**.

C.1 PROCESS MODULES OF THE CHEMICAL PRODUCTION SUBSYSTEM

This section presents the process modules associated with the chemical production subsystem. The order of presentation is as follows: **Section C.1.1** presents the model for the electrolyser process module; **Section C.1.2** presents the model for the primary dechlorination process module; **Section C.1.3** presents the model for the secondary dechlorination process module; **Section C.1.4** presents the model for the precipitation process module; **Section C.1.5** presents the model for the clarification process module; **Section C.1.6** presents the model for the primary filtration process module; **Section C.1.7** presents the model for the secondary filtration process module; **Section C.1.8** presents the model for the cation-exchange process module; **Section C.1.9** presents the model for the caustic evaporation process module; **Section C.1.10** presents the model for the hydrochloric acid synthesis process module; **Section C.1.11** presents the model for the sodium hypochlorite process module; and, **Section C.1.12** presents the model for the Hydecat destruction process module.

C.1.1 The Electrolyser Process Module

The electrolyser process module comprises elements which model the conversion of sodium chloride to products and by-products, the transfer of species across the membrane into the caustic soda solution and the processing of the chlorine and hydrogen gases produced by the electrolyser. In addition, the process module includes an element for the dosing of

hydrochloric acid to the lean brine emerging from the electrolyser. The reasons for combining the electrolyser with the hydrochloric acid dosing operation are that:

- All lean brine emerging from the electrolyser must be treated with hydrochloric acid so that any sodium hypochlorite present in the lean brine is converted to chlorine which is handled during the dechlorination stages. The removal of chlorine from the brine is required due to the sensitivity of the cation-exchange resin to oxidising species.

- The hydrochloric acid dosing is an operation dedicated to the lean brine emerging from the electrolyser. There is no other source within the system which could be reused at this point which would require this treatment.

Figure C.1 illustrates the model for the electrolyser process module. A stream key is presented in Table C.1 while the functions of the various building blocks which constitute the model are described in Table C.2. Further comments regarding the model follow these tables.
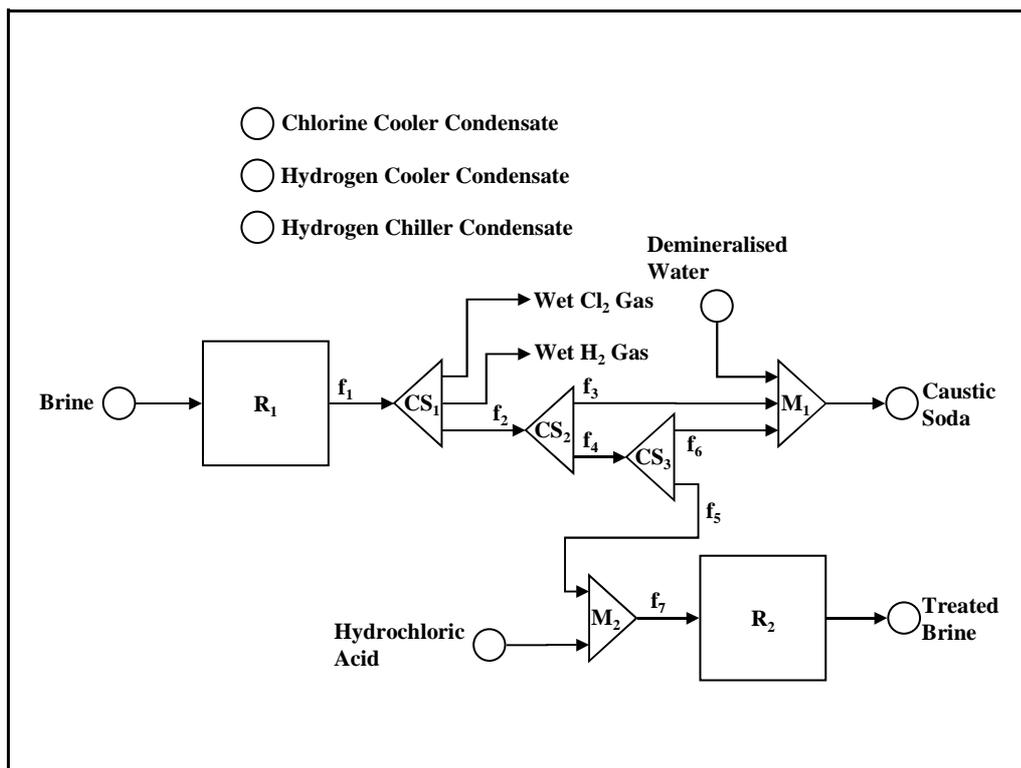
Figure C.1. *Diagram of the model for the electrolyser process module.*

Table C.1. *Stream key for the model for the electrolyser process module.*

Stream	Description
f_1	Mass flow of lean brine, reaction products and by-products from the NaCl reaction block (R_1) to the gas component separator block (CS_1).
f_2	Mass flow of liquid from the gas component separator block (CS_1) to the NaOH component separator block (CS_2).
f_3	Mass flow of NaOH and other species from the NaOH component separator block (CS_2) to the caustic soda product mixing block (M_1).
f_4	Mass flow of lean brine from the NaOH component separator block (CS_2) to the H_2O component separator block (CS_3).
f_5	Mass flow of lean brine from the H_2O component separator block (CS_3) to the hydrochloric acid mixing block (M_2).
f_6	Mass flow of species H_2O from the H_2O component separator block (CS_3) to the caustic soda product mixing block (M_1).
f_7	Mass flow of lean brine and hydrochloric acid from the hydrochloric acid mixing block (M_2) to the hypochlorite destruction reaction block (R_1).

Table C.2. *The functions of the various building blocks associated with the model for the electrolyser process module.*

Building Block	Function
CS_1	Divides the lean brine, reaction products and by-products stream (f_1) from the NaCl reaction block (R_1) into hydrogen gas, chlorine gas and a liquid stream (f_2) considered further by the model.
CS_2	Divides the liquid stream (f_2) from the gas component separator block (CS_1) into a lean brine stream (f_4) and a stream of species (f_3) which becomes part of the caustic soda product.
CS_3	Divides the lean brine stream (f_4) into the lean brine stream (f_5) which is recycled to the brine circuit and an H_2O species stream (f_6) which is sent to the caustic soda product mixing block (M_1).
M_1	Represents the combination of demineralised water, the species H_2O from the H_2O component separator block (CS_3) and the stream of species which becomes part of the caustic soda product (f_3). These streams combine to form the caustic soda which is available to the plant.
M_2	Represents the addition of hydrochloric acid to the lean brine emerging from the electrolyser.
R_1	Represents the conversion of sodium chloride to products and by-products.
R_2	Represents the destruction of sodium hypochlorite by hydrochloric acid.

The following points are noted regarding the modelling of this process module:

- While in reality the electrolyser comprises an anode and a cathode separated by a selectively permeable membrane, these elements of the operation are not transferred directly to the process module. Instead, these aspects of the system are represented in terms of a set of overall reactions, rather than separate reactions at the anode and the cathode, and the transfer of species to the various solutions. The reactions take place in the NaCl reaction block (R_1) while the distribution of species to the various streams associated with the electrolyser is represented by a series of component separators (CS_1, CS_2 and CS_3). The set of reactions taking place in the NaCl reaction block (R_1) is as follows:

$$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O \qquad\qquad C.1$$

$$3NaOCl \rightarrow NaClO_3 + 2NaCl \qquad\qquad C.2$$

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2 \qquad\qquad C.3$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad\qquad C.4$$
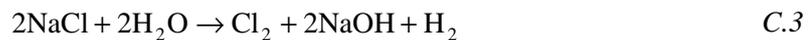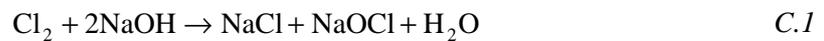
    There is a tight specification on the concentrations of the species in the brine entering the electrolyser. In particular, with the concentration of NaCl being held constant and the flowrate of brine to the electrolyser being fixed, the molar extents of the reactions taking place in the electrolyser are assumed to be the same as those associated with the current operating conditions.

- Regarding the concentrations of species in the brine entering the electrolyser, the following points are noted:

  - The concentrations of Cl_2, $MgCl_2$ and $CaCl_2$ in the brine are controlled by the cation-exchanger preceding the electrolyser. As such, the mass-loads of these species entering the electrolyser are constant; the mass-load of chlorine is assumed to be zero, that is, the residual chlorine present in the brine entering the cation-exchanger is destroyed in the cation-exchanger.

  - Concentrations of the species $NaHSO_3$, $NaOCl$, HCl, H_2, O_2, $CaCO_3$, $Mg(OH)_2$ and Insolubles in the brine entering the electrolyser are zero. The concentrations of these species have been reduced to zero either by chemical means or separation in other operations within the circuit.

- The concentrations of $NaClO_3$, $NaOH$, Na_2CO_3 and Na_2SO_4 are variable but are subject to maximum inlet concentration constraints at the inlet of the electrolyser. The concentration of H_2O is similarly variable.

- The stream emerging from the NaCl reaction block (R_1) comprises the lean brine together with the reaction products and by-products. In representing the different streams associated with the electrolyser, the species are distributed via a series of component separators. The following points are noted regarding the distribution of these species:

  - The flowrate and composition of the chlorine gas and the hydrogen gas is considered constant. This assumption is valid since all species associated with the dry gases are derived from the reactions involving H_2O and NaCl, the mass-load of the latter being fixed. The wet gas streams are separated from the stream emerging from the NaCl reaction block (R_1) at the gas component separator block (CS_1).

  - In practice, a certain quantity of caustic soda is circulated through the electrolyser. NaOH produced by the reactions taking place at the cathode concentrates this caustic soda to the strength produced at the outlet of the electrolyser. A fixed flow of the caustic soda stream produced by the electrolyser is returned to the electrolyser as a process requirement. The balance is sent to operations within the complex which either use it, or process it further.

    Given that the electrolyser is operating at steady-state, the material added to the caustic soda loop, that is, dilution water, the species generated via chemical reaction and the species transferred across the membrane, must leave the caustic soda loop via the caustic soda sent to the other operations within the complex. Thus, in modelling the caustic soda side of the electrolyser, the caustic soda loop is not considered at all. Instead the production of the caustic soda stream which is sent to the complex is represented as a blending of the dilution water and the species produced by reaction and transferred across the selectively permeable membrane in the electrolyser.

    In considering the transfer of these species, the following assumptions are made:

    - With the mass-load of $MgCl_2$, $CaCl_2$ and NaCl in the brine being constant, the transfer of these species is modelled as a fixed mass of species transferred to the caustic soda. The

transfer of $NaClO_3$ is also represented by a fixed mass-load transferred to the caustic soda.

    – With the mass-load of Na_2SO_4 and Na_2CO_3 in the brine being variable, a fixed proportion is assumed to be transferred to the caustic soda.

    – The transfer of Cl_2 and NaOCl across the membrane is assumed to be negligible. H_2 and O_2 are present exclusively in the gas phase.

    – It is assumed that there is no NaOH present in the lean brine stream. The species H_2O is transferred to the caustic soda such that the concentration of NaOH in the caustic soda produced by the electrolyser is equivalent to that of the existing configuration.

In the model for the electrolyser process module, the transfer of all species, excluding water (H_2O), takes place at NaOH component separator block (CS_2). The water transferred to the caustic soda in the electrolyser is removed from the lean brine stream at the H_2O component separator block (CS_3). The transferred H_2O species, the dilution water added to the circuit and the species transferred across the membrane are blended to produce the caustic soda product from the electrolyser at the caustic soda product mixing block (M_1).

- The gas streams emerging from the electrolyser are saturated with water and undergo further processing to remove this water. With the species concentrations and flowrates of the wet gas streams being constant, the species concentrations and flowrates of the condensate sources are assumed to be constant. These condensate sources are modelled as primary sources with fixed concentrations and fixed flowrates; the operations which produce these condensate sources are not considered. The gas streams leaving the electrolyser are similarly not integrated with the superstructure. In the case of hydrogen gas, no other sources of hydrogen gas are available on the complex. It is thus excluded from the Pinch Analysis since any demand for hydrogen gas must be satisfied using this source. With there being a number of different sources of chlorine however, the chlorine gas is included in the model as a primary source of fixed species concentration.

- In modelling the dosing of hydrochloric acid to the lean brine, the assumption is made that the molar ratio of hydrochloric acid to sodium hypochlorite in the lean brine must be the same as the ratio currently supplied. It is noted that the dosing is not modelled as a fixed addition of concentrated hydrochloric acid even though the mass-load of sodium hypochlorite present in the lean brine is

constant. Representing the dosing operation in terms of the molar ratio of hydrochloric acid to sodium hypochlorite allows the possibility of reusing other HCl-containing sources present on the complex. Clearly, HCl is modelled as a desirable species in this situation.

C.1.2 The Primary Dechlorination Process Module

Figure C.2 shows the model for the primary dechlorination process module. Table C.3 presents a stream key for the process module while the functions of the various building blocks from which the model is assembled are presented in Table C.4. Comments on the model follow these tables.
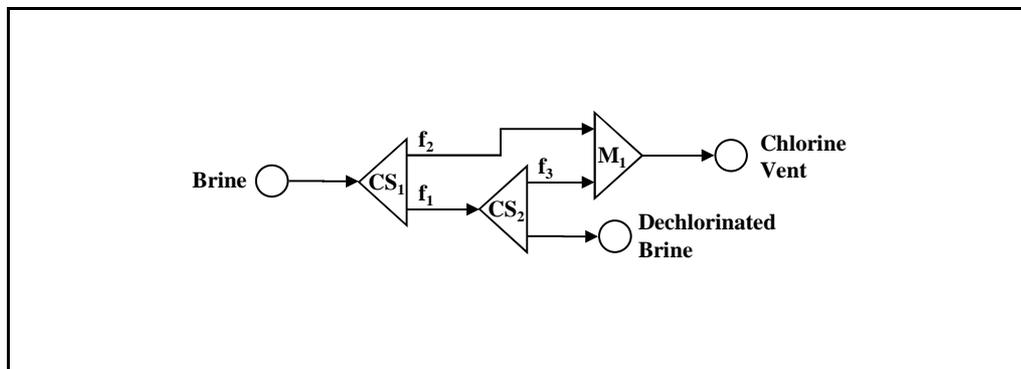
Figure C.2. *Diagram of the model for the primary dechlorination process module.*

Table C.3. *Stream key for the model for the primary dechlorination process module.*

Stream	Description
f_1	Lean brine from the H_2O component separator block (CS_1) to the Cl_2 component separator block (CS_2).
f_2	Mass flow representing the water removed from the brine by the air passing through the primary dechlorinator.
f_3	Mass flow of chlorine from the Cl_2 component separator block (CS_2) to the chlorine vent mixing block (M_1).

Table C.4. *The functions of the various building blocks associated with the model for the primary dechlorination process module.*

Building Block	Function
CS_1	Represents the removal of water from the brine by the air passing through the dechlorinator.
CS_2	Represents the removal of chlorine from the brine by the air passing through the dechlorinator.
M_1	Represents the combination of water and chlorine removed from the brine by the air passing through the dechlorinator.

The primary dechlorinator is modelled as a separate process module, that is, it is not incorporated with the electrolyser process module, even though it is a process requirement that the brine from the electrolyser pass directly through this stage. In the existing configuration of the plant, condensate from the chlorine cooler, which contains a residual quantity of Cl_2, is combined with the brine stream prior to the primary dechlorination stage; the sodium hypochlorite synthesis plant could serve as an alternate destination for this source, if economically feasible. Hence, with the existence of these two possibilities, that is, that the chlorine condensate could be sent to the primary dechlorinator or to the sodium hypochlorite synthesis plant, it is necessary to represent the two process modules separately.

The primary dechlorinator uses air to strip chlorine from the brine stream. Alongside the removal of chlorine, water is also removed from the brine. The quantity of water removed from the brine is assumed to be the same as that currently removed by the dechlorinators and is represented via the H_2O component separator block (CS_1). The removal of chlorine is represented by a removal ratio and is separated from the lean brine at the Cl_2 component separator block (CS_2); this removal ratio is assumed equivalent to that currently achieved on the plant. The chlorine vent mixing block (M_1) combines the chlorine and water removed from the brine stream at the component separator blocks.

It should be noted that the air stream used in the primary dechlorination step is not represented in the process module since the association of this stream with the dechlorinator will not be different in the optimised scenario.

C.1.3 The Secondary Dechlorination Process Module

Figure C.3 shows the model for the secondary dechlorination process module. A stream key for the process module is presented in Table C.5 while the functions of the various building blocks associated with the process module are described in Table C.6. Comments on the model follow these tables.
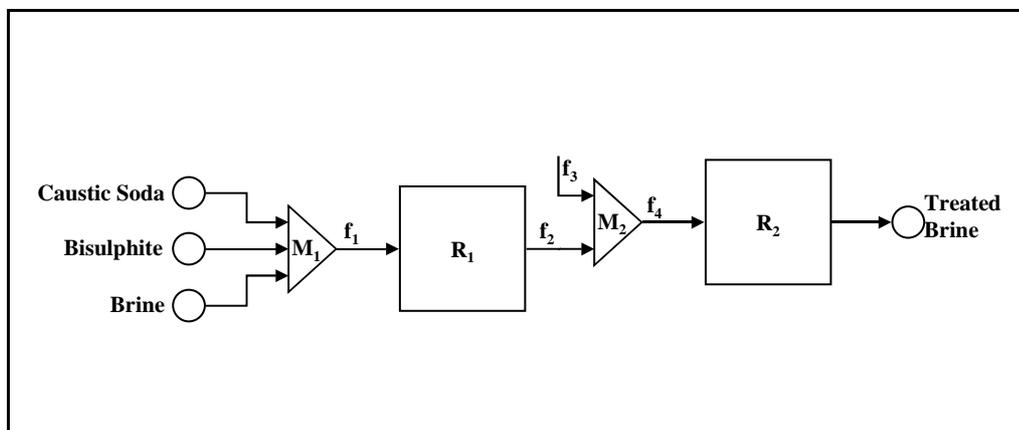
Figure C.3. *Diagram of the model for the secondary dechlorination process module.*

Table C.5. *Stream key for the model for the secondary dechlorination process module.*

Stream	Description
f_1	Mass flow of brine, caustic soda and sodium bisulphite to the dechlorination reaction block (R_1).
f_2	Mass flow of brine from the dechlorination reaction block (R_1) to the oxygen mixing block (M_2).
f_3	Mass flow of oxygen for the conversion of bisulphite to sulphate. This is a modelling approximation.
f_4	Mass flow of brine and oxygen to the bisulphite destruction reaction block (R_1)

Table C.6. *The functions of the various building blocks associated with the model for the secondary dechlorination process module.*

Building Block	Function
M_1	Represents the combination of brine, caustic soda and sodium bisulphite.
M_2	Represents the combination of the dechlorinated brine with a stoichiometric quantity of oxygen required for the conversion of the residual bisulphite to sulphate. This element of the process module is purely a modelling approximation.
R_1	Represents the neutralisation of hydrochloric acid present in the brine by caustic soda and the destruction of chlorine present in the brine by sodium bisulphite.
R_2	Represents the conversion of sodium bisulphite to sodium sulphate. This element of the process module is a modelling approximation.

While all the brine from the primary dechlorination process module is routed to the secondary dechlorination process module, the secondary dechlorination step is modelled as a separate process module. This incorporates the possibility into the superstructure that the condensate from the chlorine cooler might bypass the primary dechlorination step and be introduced at the secondary dechlorination stage, if economically feasible. The significant areas of the model are as follows:

- Excess hydrochloric acid present in the brine stream coming from the primary dechlorination stage is neutralised by the addition of caustic soda to the brine (Equation C.5). Residual chlorine present in the brine following the primary dechlorination stage is destroyed by the addition of sodium bisulphite (Equation C.6).

$$HCl + NaOH \rightarrow NaCl + H_2O \qquad\qquad C.5$$

$$Cl_2 + 3NaOH + NaHSO_3 \rightarrow Na_2SO_4 + 2NaCl + 2H_2O \qquad\qquad C.6$$
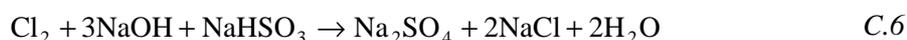
These two reactions are represented in the dechlorination reaction block (R_1). Clearly, NaOH is modelled as a desirable species at the caustic soda inlet to the process module while $NaHSO_3$ is modelled as a desirable species at the sodium bisulphite inlet to the process module. The neutralisation reaction is complete with respect to hydrochloric acid while the outlet from the reaction block is considered to have a residual concentration of chlorine and sodium bisulphite. These residual concentrations are assumed to be the same as those for the current operating conditions.

- While there is a residual load of sodium bisulphite present in the brine leaving the secondary dechlorination stage, the assumption is made that this load is converted to sodium sulphate as the brine is recycled to the electrolyser. A second reaction block (R_2) is used to represent this conversion reaction which proceeds according to:

$$NaOH + NaHSO_3 + 0.5O_2 \rightarrow Na_2SO_4 + H_2O \qquad C.7$$

In the model, a stoichiometric quantity of oxygen (f_3) is added to the brine entering the bisulphite destruction reaction block (R_2) such that Equation C.7 is balanced. The brine leaving the secondary dechlorination process module is modelled such that it contains no sodium bisulphite.

C.1.4 The Precipitation Process Module

The precipitation process module has already been considered in some detail in **Chapter 5**; it is considered here only briefly. Figure C.4 shows the model for the precipitation process module. The stream key is presented in Table C.7 while the functions of the building blocks which make up the model are presented in Table C.8.
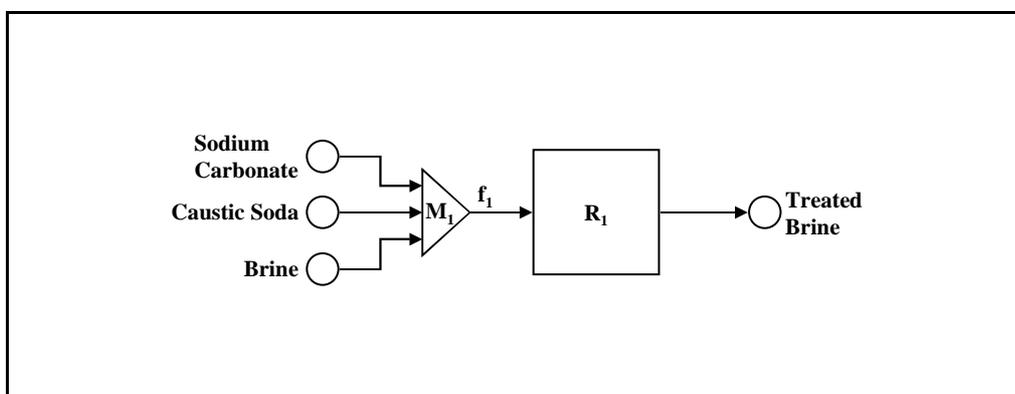

Figure C.4. *Diagram of the model for the precipitation process module.*

Table C.7. *Stream key for the model for the precipitation process module.*

Stream	Description
f_1	Mass flow of brine, sodium carbonate and caustic soda to the precipitation reaction block (R_1).

Table C.8. *The functions of the various building blocks associated with the model for the precipitation process module.*

Building Block	Function
M_1	Represents the combination of brine, sodium carbonate and caustic soda.
R_1	Represents the precipitation of calcium carbonate and magnesium hydroxide.

C.1.5 The Clarification Process Module

Figure C.5 shows the model for the clarification process module. A stream key is presented in Table C.9 while the functions of the various building blocks which constitute the model are described in Table C.10. Some comments on the model follow these tables.
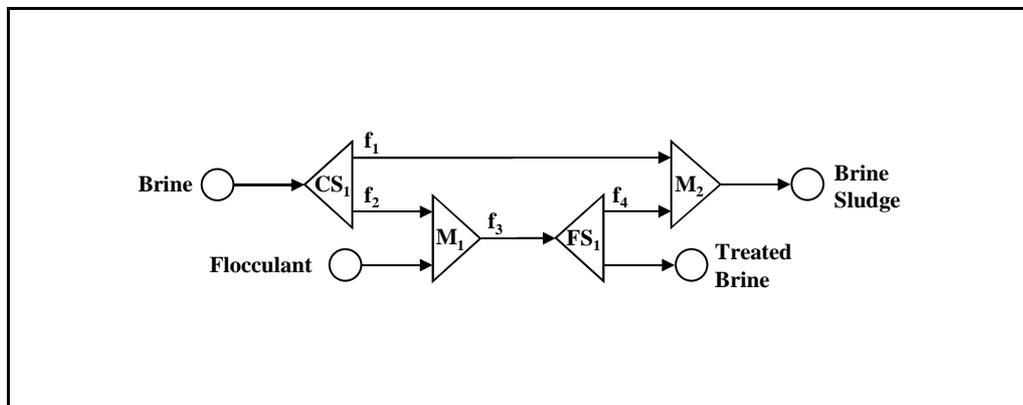
Figure C.5. *Diagram of the model for the clarification process module.*

Table C.9. *Stream key for the model for the clarification process module.*

Stream	Description
f_1	Mass flow of solids removed from the brine by the solids component separator block (CS_1) to the brine sludge mixing block (M_2).
f_2	Mass flow of clarified brine to the flocculant addition mixing block (M_1).
f_3	Mass flow of brine and flocculant to the brine liquid flow separator (FS_1).
f_4	Mass flow of brine from the brine liquid flow separator (FS_1) to the brine sludge mixing block (M_2).

Table C.10. *The functions of the various building blocks associated with the model for the clarification process module.*

Building Block	Function
FS_1	Divides the clarified brine into two streams. One stream becomes part of the brine sludge removed from the clarifier (f_4) while the other is made available to the superstructure.
CS_1	Effects the removal of solids from the brine according to the different removal ratios.
M_1	Combines the clarified brine with the flocculant. Only the dilution water associated with the flocculant is represented in the model.
M_2	Combines the solids removed from the brine and the liquid portion which becomes part of the brine sludge which was separated by the brine liquid flow separator block (FS_1).

The brine sludge comprises a liquid component and a solids component. Its flow is considered to be variable but the percentage of solids is constant. The separation of the brine sludge from the brine is thus represented by the solids component separator block (CS_1) which contributes the solid component of the brine sludge stream and the brine liquid flow separator block (FS_1) which contributes the liquid component of the brine sludge. These two streams are combined at the brine sludge mixing block (M_2). The following additional points are noted regarding the model:

- Complete removal of calcium carbonate and magnesium hydroxide and partial removal of Insolubles is assumed at the solids component separator block (CS_1).

- The dosing of flocculant is modelled as being proportional to the quantity of solids removed from the brine. This ratio is derived from existing plant records. The actual flocculant is not considered in the model and the assumption is made that it is completely removed during the clarification and filtration stages at negligible cost. The addition of flocculant is thus represented as the addition of the dilution water accompanying the flocculant. To account for the cost associated with the use of the flocculant however, an appropriate cost factor is attached to the flocculant inlet to the process module.

- The concentration profile of the liquid component of the brine sludge is assumed to be the same as the clarified brine.

C.1.6 The Primary Filtration Process Module

All assumptions associated with the model for the primary filtration process module have been presented in **Chapter 5**; the process module is considered here only briefly. Figure C.6 shows the model for the primary filtration process module. The stream key and the functions of the various building blocks associated with the process module are presented in Table C.11 and Table C.12 respectively.
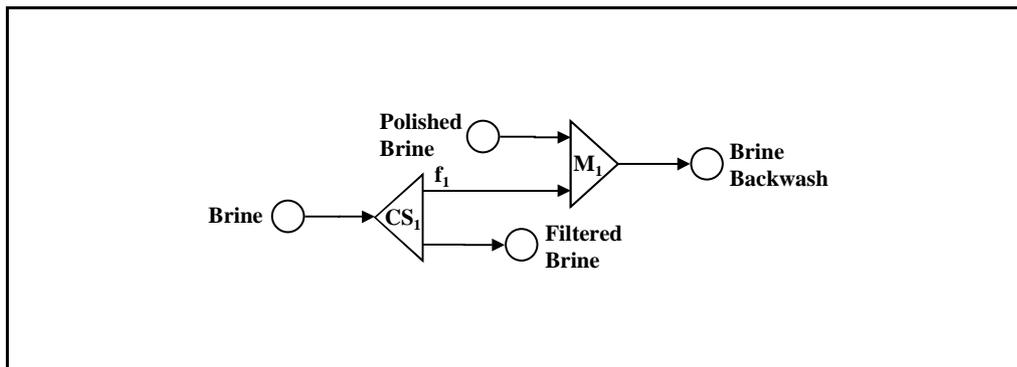
Figure C.6. *Diagram of the model for the primary filtration process module.*

Table C.11. *Stream key for the model for the primary filtration process module.*

Stream	Description
f_1	Mass flow of solids removed during the normal cycle of operation transferred to the backwash cycle of operation.

Table C.12. *The functions of the various building blocks associated with the model for the primary filtration process module.*

Building Block	Function
CS_1	Effects the removal of solids from the brine during the normal cycle of operation.
M_1	Represents the combination of solids from the normal cycle of operation with the brine used for backwashing the filter.

C.1.7 The Secondary Filtration Process Module

All assumptions associated with the model for the secondary filtration process module have been presented in **Chapter 5**; the process module is considered here only briefly. Figure C.7 shows the model for the secondary filtration process module. The stream key is presented in Table C.13 while Table C.14 describes the functions of the various building blocks which constitute the process module.
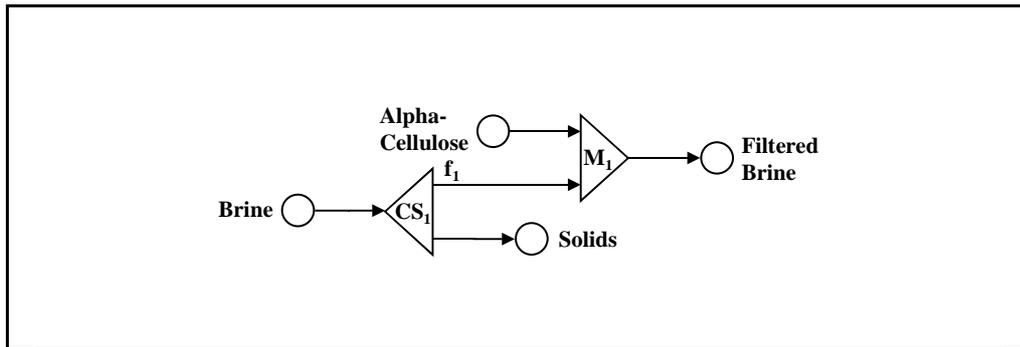
Figure C.7. *Diagram of the model for the secondary filtration process module.*

Table C.13. *Stream key for the model for the secondary filtration process module.*

Stream	Description
f_1	Mass flow of brine following solids removal to the alpha-cellulose dilution water mixing block (M_1).

Table C.14. *The functions of the various building blocks associated with the model for the secondary filtration process module.*

Building Block	Function
CS_1	Represents the removal of solids from the brine by the filter.
M_1	Represents the combination of the brine with the dilution water used for the alpha-cellulose addition.

C.1.8 The Cation-Exchange Process Module

Figure C.8 shows the model for the cation-exchange process module. Both the normal cycle of operation and the regeneration cycle of operation are included in the model. As such there are several similarities between this model and the model presented for the demineralisation plant process module in **Chapter 5**. Where these similarities occur, the arguments presented during the analysis of the demineralisation plant will be referenced as being applicable. Table C.15 presents the stream key associated with this process module while Table C.16 describes the functions of the various building blocks which make up the process module. Comments on this model follow these tables.

Figure C.8. *Diagram of the model for the cation-exchange process module.*

Table C.15. *Stream key for the model for the cation-exchange process module.*

Stream	Description
f_1	Mass flow of sodium ions associated with the destruction of chlorine in the brine.
f_2	Mass flow of brine from the chlorine destruction reaction block (R_1).
f_3	Mass flow of NaCl which substitutes the $MgCl_2$ and $CaCl_2$ in the brine.
f_4	Mass flow of ions, removed as salts, transferred from the normal cycle of operation to the regeneration sequence.
f_5	Mass flow of demineralised water to Brine Displacement stage (IXR1).
f_6	Mass flow of demineralised water, representing the hold-up from the Backwash stage, to the Acid Regeneration stage (IXR3).
f_7	Mass flow of demineralised water to the Acid Rinse stage (IXR4).
f_8	Mass flow of demineralised water, representing the hold-up from the Acid Rinse stage, to the Caustic Regeneration stage (IXR5).
f_9	Mass flow of demineralised water to the Caustic Rinse stage (IXR6).
f_{10}	Mass flow of demineralised water, representing the hold-up from the Caustic Rinse stage, to the Brine Replacement stage (IXR7).
f_{11}	Mass flow of polished brine, representing the hold-up from the normal cycle of operation of the cation-exchanger, to the Brine Displacement stage (IXR1).
f_{12}	Mass flow of polished brine to the Brine Replacement stage (IXR7).
f_{13}	Mass flow of hydrochloric acid to the Acid Regeneration stage (IXR3).
f_{14}	Mass flow of hydrochloric acid, representing the hold-up from the Acid Regeneration stage, to the Acid Rinse stage (IXR4).
f_{15}	Mass flow of hydrochloric acid, ions (as salts) and demineralised water to the Acid Regeneration stage HCl component separator block (CS_2).
f_{16}	Mass flow of HCl species consumed during Acid Regeneration stage (IXR3).
f_{17}	Mass flow of H_2O species to the Caustic Regeneration stage (IXR5). This represents the generation of H_2O during the conversion of the cation-exchange resin from the hydrogen form to the sodium form.
f_{18}	Mass flow of caustic soda to the Caustic Regeneration stage (IXR5).
f_{19}	Mass flow of caustic soda, representing the hold-up from the Caustic Regeneration stage, to the Caustic Rinse stage (IXR6).
f_{20}	Mass flow of caustic soda, H_2O species and demineralised water to the Caustic Regeneration stage NaOH component separator block (CS_3).
f_{21}	Mass flow of NaOH species consumed during the Caustic Regeneration stage (IXR6).

Table C.16. *The functions of the various building blocks associated with the model for the cation-exchange process module.*

Building Block	Function
FS_1	Divides the flow of polished brine between the Brine Displacement stage (f_{11}) and the Brine Replacement stage (f_{12})
FS_2	Divides the flow of hydrochloric acid between the Acid Regeneration stage (f_{13}) and the Acid Rinse stage (f_{14}).
FS_3	Divides the flow of demineralised water between the different stages of the regeneration sequence. f_5 is sent to the Brine Displacement stage; f_6 is sent to the Acid Regeneration stage; f_7 is sent to the Acid Rinse stage; f_8 is sent to the Caustic Regeneration stage; f_9 is sent to the Caustic Rinse stage; and, f_{10} is sent to the Brine Replacement stage.
FS_4	Divides the flow of caustic soda between the Caustic Regeneration stage (f_{18}) and the Caustic Rinse stage (f_{19}).
CS_1	Separates the ions, as salts, from the brine passing through the cation-exchanger.
CS_2	Removes a mass-load of HCl species equivalent to the ionic load removed by the cation-exchanger during the normal cycle of operation.
CS_3	Removes a mass-load of NaOH species equivalent to the ionic load removed by the cation-exchanger during the normal cycle of operation.
M_1	Combines the mass-load of NaCl species, which substitutes for the $MgCl_2$ and $CaCl_2$ in the brine, with the brine stream being treated by the cation-exchanger.
M_2	Combines the polished brine hold-up from the normal cycle of operation with the demineralised water sent to the Brine Displacement stage to produce the effluent from the Brine Displacement stage (IXR1).
M_3	Combines the hydrochloric acid, ions (salts) removed during the normal cycle of operation and the demineralised water hold-up from the Backwash stage for the Acid Regeneration stage (IXR3).
M_4	Combines the hydrochloric acid hold-up from the Acid Regeneration stage and the demineralised water for the Acid Rinse stage to produce the effluent from the Acid Rinse stage (IXR4).
M_5	Combines the caustic soda, H_2O species (which represent the H_2O species generated from the conversion of the cation-exchange resin from the hydrogen form to the sodium form) and the demineralised water hold-up from the Acid Rinse stage for the Caustic Regeneration stage (IXR5).
M_6	Combines the caustic soda hold-up from the Caustic Regeneration stage and the demineralised water for the Caustic Rinse stage to produce the effluent from the Caustic Rinse stage (IXR6).
M_7	Combines the demineralised water hold-up from the Caustic Rinse stage and the polished brine from the Brine Replacement stage to produce the effluent from the Brine Replacement stage (IXR7).
R_1	Associated with the destruction of the chlorine present in the brine being treated by the cation-exchanger.

One difference between the demineralisation plant process module and the cation-exchange process module is the way in which the initial hold-up from the normal operating cycle to the regeneration cycle is modelled. In the demineralisation plant process module, raw water entered the process module through a single inlet. This stream was split into three to represent the feed to the normal cycle of operation, the hold-up from the normal cycle of operation to the regeneration cycle and the effluent of the final stage. With the quality associated with each of these splits having to be the same, and the raw water being a combination of two different sources of water, the ratio of which was determined during the optimisation, the situation had to be modelled in this way. For the cation-exchanger however, there is only one source of brine that can be used for the normal cycle of operation and the regeneration cycle. Thus it is not necessary to model the situation as a split of a single stream entering the process module. Instead the connectivity matrix is used to ensure that the quality of brine entering the normal cycle of operation and the regeneration cycle are identical.

In practice, the exchange of divalent cations with the cation-exchange resin proceeds according to the reaction:

$$2NaX + MCl_2 \rightarrow MX_2 + 2NaCl \qquad \qquad C.8$$

where X represents a structural unit of the cation-exchange resin and MCl_2 represents divalent chloride. NaX is the cation-exchange resin in the sodium form and MX_2 is the cation-exchange resin in the divalent cation form. The divalent chloride from the brine is thus substituted stoichiometrically by sodium chloride. The cation-exchange resin is converted from the sodium form to the divalent cation form. The reaction for the Acid Regeneration step proceeds according to the reaction:

$$MX_2 + 2HCl \rightarrow 2HX + MCl_2 \qquad \qquad C.9$$

where HX is the hydrogen form of the cation-exchange resin. In this step, a mass-load of hydrogen chloride is destroyed and a stoichiometric quantity of divalent chloride appears in the hydrochloric acid stream leaving the Acid Regeneration stage. The cation-exchange resin is converted from the divalent cation form to the hydrogen form. The reaction for the Caustic Regeneration step proceeds as:

$$HX + NaOH \rightarrow NaX + H_2O \qquad \qquad C.10$$

Here a mass-load of sodium hydroxide is destroyed and a stoichiometric quantity of H_2O is added to the caustic soda stream leaving the regeneration stage. The cation-exchange resin is converted from the hydrogen form to the sodium form.

If the resin-species complexes are ignored in the above reactions (Equations C.8-C-10), it is possible to represent these steps in terms of species substitutions rather than species transformations. For the normal cycle of operation, MCl_2 is substituted with NaCl. This is

achieved via the NaCl substitution mixing block (M_1) and the divalent chloride component separator block (CS_1). The MCl_2 eliminated from the brine stream is sent to the Acid Regeneration stage mixing block (M_3) while a stoichiometric quantity of HCl species is eliminated from the hydrochloric acid stream at the HCl component separator block (CS_2). Similarly, a stoichiometric quantity of H_2O species is added to the dilute caustic soda entering the Caustic Regeneration stage mixing block (M_5) and a stoichiometric quantity of NaOH species is removed at the NaOH component separator block (CS_3).

It should be noted that the stoichiometric quantity involved in these substitutions corresponds to the total ionic load removed by the cation-exchanger during the normal cycle of operation, that is, the divalent cations and the residual chlorine present in the brine stream. The assumption is made that all Cl_2 present in the brine entering the normal cycle of operation of the cation-exchanger is converted to sodium chloride. This reaction proceeds according to:

$$2Na^+ + Cl_2 \rightarrow 2NaCl \qquad\qquad C.11$$

In modelling this aspect, a stoichiometric quantity of Na^+ cations (f_3) is introduced into the chlorine destruction reaction block (R_1). This stream of Na^+ cations corresponds to the Na^+ cations removed from the cation-exchange resin by chlorine.

In determining the ionic load removed by the cation-exchanger, the concentration of calcium chloride and magnesium chloride in the brine emerging from the cation-exchanger are assumed to be at the levels achieved in the existing scenario. Complete destruction of chlorine is assumed. As was the case with the demineralisation plant process module, potential changes in the regeneration frequency associated with this ionic load are accounted for by scaling the amounts of material required for the regeneration according to a reference.

In **Chapter 5**, a number of potential reuse opportunities were identified for the effluents associated with the regeneration sequence of the cation-exchanger. These opportunities were identified by an analysis of the passage of fluid through the regeneration sequence similar to that presented for the demineralisation plant process module. This analysis is presented as follows:

- **Changeover:**

    The cation-exchanger comprises two resin beds arranged in series. When the changeover from the normal cycle of operation to the regeneration cycle is made, one of the beds is taken off-line and the regeneration procedure commences. At the changeover, the resin bed contains brine from the polishing (secondary) filter.

- **Brine Displacement Stage:**

  During the Brine Displacement stage, demineralised water is used to displace the polished brine from the resin bed. At the end of this stage, the bed contains only demineralised water and the effluent produced from the stage is a weak brine solution.

- **Backwash Stage:**

  The Backwash stage sees the resin bed being flushed with demineralised water in the opposite direction to the normal flow. At the conclusion of this stage, the bed contains only demineralised water and the effluent from the stage is considered to be demineralised water.

- **Acid Regeneration Stage:**

  During the Acid Regeneration stage, hydrochloric acid, at the required concentration, is introduced into the resin bed and displaces the demineralised water hold-up from the previous stage. Simultaneously, the divalent cations removed during the normal cycle of operation are eluted from the resin which is converted to the hydrogen form according to Equation C.9. At the end of the stage, the bed contains only hydrochloric acid at the concentration at which it was supplied to the stage; the effluent is a mixture of the demineralised water hold-up from the Backwash stage, the hydrochloric acid that has passed through the bed and the divalent cations eluted from the cation-exchange resin.

- **Acid Rinse Stage:**

  During the Acid Rinse stage, demineralised water is used to displace the hydrochloric acid hold-up from the Acid Regeneration stage. At the conclusion of the stage, the resin bed contains only demineralised water while the effluent is a weak hydrochloric acid solution.

- **Caustic Regeneration Stage:**

  Caustic soda at the required concentration is used in the Caustic Regeneration stage and displaces the demineralised water hold-up from the Acid Rinse stage. The resin is converted from the hydrogen form to the sodium form with the generation of H_2O species according to Equation C.10. At the end of this stage, the resin bed contains caustic soda at the influent concentration while the effluent is a dilute caustic soda solution.

- **Caustic Rinse Stage:**

    Demineralised water is used in the Caustic Rinse stage to displace the caustic soda hold-up from the Caustic Regeneration stage. At the conclusion of this stage, the resin bed contains only demineralised water while the effluent is a weak caustic soda solution.

- **Brine Replacement Stage:**

    During the Brine Replacement stage, brine from the polishing filter is used to displace the demineralised water hold-up from the Caustic Rinse stage. At the end of the stage, the resin bed volume is occupied with the polished brine and the resin bed is placed back on-line. The effluent from this stage is a weak brine solution.

In modelling the various stages for the regeneration sequence, the hold-up volumes associated with the various stages are modelled in the same way as that for the demineralisation plant process module. Table C.17 presents a list of the building blocks associated with each of the regeneration stages.

Table C.17. *The building blocks associated with various stages of the cation-exchange regeneration sequence.*

Regeneration Stage	Building Blocks
Brine Displacement	FS_1, FS_3, M_2
Backwash	FS_3
Acid Regeneration	FS_2, FS_3, M_3, CS_2
Acid Rinse	FS_2, FS_3, M_4
Caustic Regeneration	FS_3, FS_4, M_5, CS_3
Caustic Rinse	FS_3, FS_4, M_6
Brine Replacement	FS_1, FS_3, M_7

Similar arguments to those presented for the demineralisation plant process module on the inclusion of concentration profiles in the model are applicable to the cation-exchange process module.

C.1.9 The Caustic Evaporation Process Module

Figure C.9 presents the model for the caustic evaporation process module. Table C.18 presents the stream key while Table C.19 describes the functions of the various building blocks associated with the process module. Some comments on the model follow these tables.
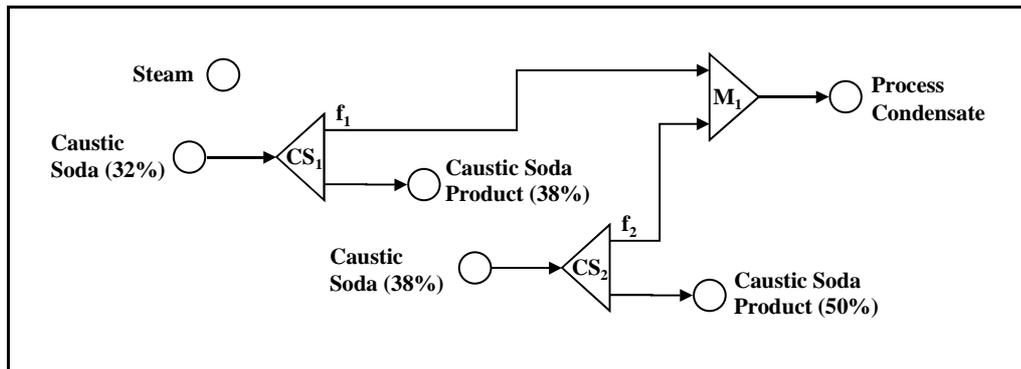
Figure C.9. *Diagram of the model for the caustic evaporation process module.*

Table C.18. *Stream key for the model for the caustic evaporation process module.*

Stream	Description
f_1	Mass flow of process condensate from the first effect of the caustic evaporation plant to the condensate mixing block (M_1).
f_2	Mass flow of process condensate from the second effect of the caustic evaporation plant to the condensate mixing block (M_2).

Table C.19. *The functions of the various building blocks associated with the model for the caustic evaporation process module.*

Building Block	Function
CS_1	Represents the first effect of the caustic evaporation plant.
CS_2	Represents the second effect of the caustic evaporation plant.
M_1	Represents the combination of process condensate from the first and second effects of the caustic evaporation plant.

The following points are raised with regard to the model:

- The dual effect caustic evaporation plant is represented as two component separator blocks, each of which produces a source of concentrated caustic soda which is available to the superstructure. The possibility is therefore introduced that the caustic soda from the first effect can be used within the system, if such use is economically feasible.

- Condensate is removed from the caustic soda at the component separator blocks as a stream of H_2O species. However, from the superstructure perspective, this condensate source is modelled as a primary source with a quality equivalent to demineralised water. It is noted that this may not be the case in practice and the quality of the water may be slightly poorer than that of demineralised water. The condensate is currently used as make-up water to the resaturator on the brine circuit.

- Steam is used as the heating medium for the first effect. The amount of steam required is modelled as being proportional to the caustic soda entering the first effect. This ratio is derived from existing plant records. This steam is supplied by UOS and condenses such that it becomes available for use by other operations in the complex. It is thus represented as a primary source with a quality equivalent to that of demineralised water. Again, this may not be the case in practice and the quality may be lower than that of demineralised water. This condensate is also currently used as make-up water to the resaturator on the brine circuit.

C.1.10 The Hydrochloric Acid Synthesis Process Module

The assumptions associated with the model for the hydrochloric acid synthesis process module have been presented in **Chapter 5**; the process module is considered here only briefly. Figure C.10 shows the model for the hydrochloric acid synthesis process module. The stream key is presented in Table C.20 while Table C.21 describes the functions of the various building blocks which constitute the process module.
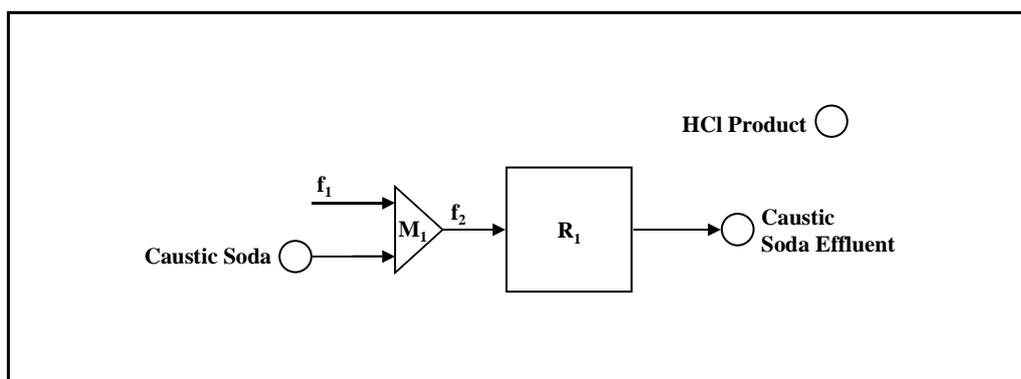
Figure C.10. *Diagram of the model for the hydrochloric acid synthesis process module.*

Table C.20. *Stream key for the model for the hydrochloric acid synthesis process module.*

Stream	Description
f_1	Mass flow representing the mass-load of hydrogen chloride to the hydrogen chloride scrubber.
f_2	Mass flow of caustic soda and hydrogen chloride to the hydrogen chloride destruction reaction block (R_1).

Table C.21. *The functions of the various building blocks associated with the model for the hydrochloric acid synthesis process module.*

Building Block	Function
M_1	Combines the gaseous hydrogen chloride load to the hydrogen chloride scrubber with the caustic soda.
R_1	Represents the reaction between caustic soda and hydrogen chloride.

C.1.11 The Sodium Hypochlorite Synthesis Process Module

The assumptions associated with the model for the sodium hypochlorite synthesis process module have been presented in **Chapter 5**. There are no internal streams or building blocks associated with this process module. The model consists of a fixed flow demand at which the species NaOH and Cl_2 are considered to be desirable. The waste sodium hypochlorite is represented as a fixed flow primary source.

C.1.12 The Hydecat Destruction Process Module

Figure C.11 shows the model for the Hydecat destruction process module. A stream key is provided in Table C.22 while the functions of the different functional units which constitute the process module are described in Table C.23
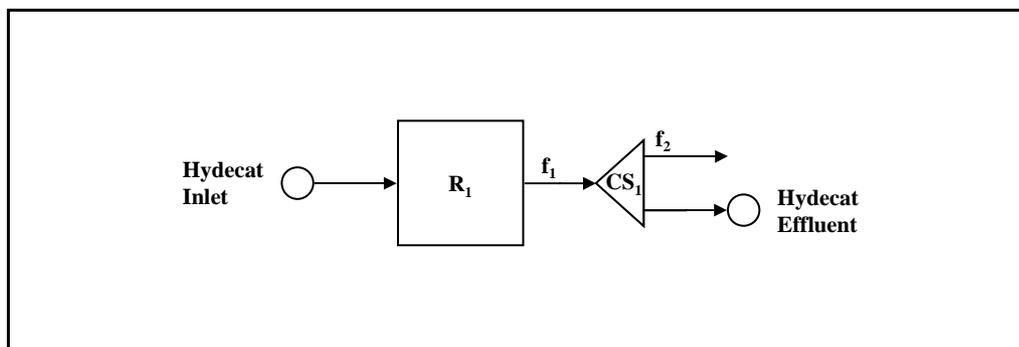
Figure C.11. *Diagram of the model for the Hydecat destruction process module.*

Table C.22. *Stream key for the model for the Hydecat destruction process module.*

Stream	Description
f_1	Mass flow of Hydecat effluent and oxygen liberated from the destruction of sodium hypochlorite to the gas component separator block (CS_1).
f_2	Mass flow of oxygen liberated from the destruction of sodium hypochlorite.

Table C.23 *The functions of the various building blocks associated with the model for the Hydecat destruction process module.*

Building Block	Function
CS_1	Divides the stream emerging from the hypochlorite destruction reaction block (R_1) into an oxygen stream and an effluent stream.
R_1	Represents the destruction of sodium hypochlorite in the Hydecat destruction plant.

The reaction for the destruction of sodium hypochlorite proceeds according to:

$$2NaOCl \rightarrow 2NaCl + O_2 \qquad \qquad C.12$$

The separation of the O_2 generated by the reaction and the effluent is represented by the component separator (CS_1).

C.2 THE COOLING TOWER PROCESS MODULE

The assumptions associated with the model for the cooling tower process module have been presented in **Chapter 5**; the process module is considered here only briefly. Figure C.12 shows the model for the cooling tower process module. Table C.24 presents a stream key for the process module while Table C.25 presents a description of the functions of the various building blocks which make up the model.
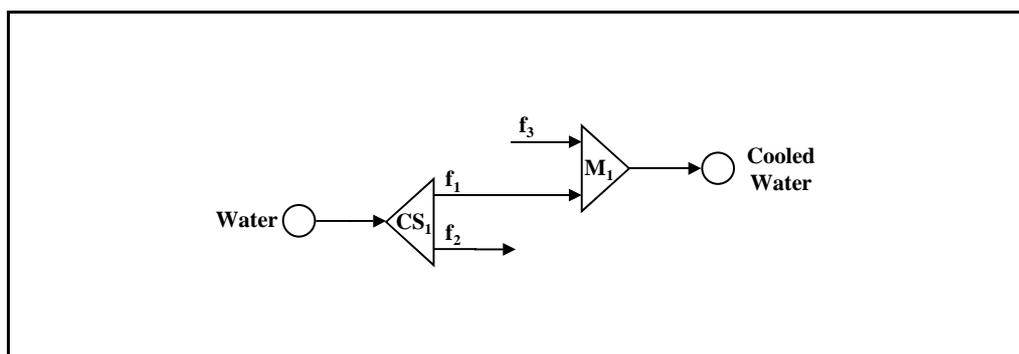
Figure C.12. *Diagram of the model for the cooling tower process module.*

Table C.24. *Stream key for the model for the cooling tower process module.*

Stream	Description
f_1	Mass flow of water from the evaporation component separator block (CS_1) to the carbon dioxide absorption mixing block (M_1).
f_2	Mass flow of evaporated water from the evaporation component separator block (CS_1).
f_2	Mass flow of Na_2CO_3 species representing the absorption of carbon dioxide from the atmosphere.

Table C.25 *The functions of the various building blocks associated with the model for the cooling tower process module.*

Building Block	Function
CS_1	Divides the water stream entering the cooling tower into an evpaporated water stream (f_2) and a water stream which is sent to the carbon dioxide mixing block (M_1).
M_1	Combines the mass-load of sodium carbonate, which represents the carbon dioxide absorbed from the atmosphere, and the water from the evaporation component separator block (CS_1).

C.3 CONCLUDING REMARKS

This appendix has presented the models for the various process modules associated with the chemical production subsystem and the cooling circuit subsystem in greater detail. The full mathematical descriptions of these models are presented in the GAMS coding included on the **CD** which accompanies this thesis.

D

MATERIAL REUSE MATRICES

Appendix D presents the material reuse matrices which show the routing of materials between the various sources and sinks associated with the different subsystems; these matrices are derived from the solution provided by the optimisation algorithm for the various subsystems. The connectivity matrix, which shows the set of possible connections between the sources and sinks of the superstructure is superimposed on the reuse matrix. The order of presentation of these matrices is as follows: Table D.1 presents the reuse matrix for the demineralisation plant subsystem in isolation from the other subsystems; Table D.2 presents the reuse matrix for the chemical production subsystem in isolation from the other subsystems. Only those elements which were included in the optimisation are shown in this table; Table D.3 presents the material use matrix for those elements which were not included in the optimisation of the chemical production subsystem. This matrix is derived from the mass-balances presented in **Appendix A**; Table D.4 presents the reuse matrix for the cooling circuit subsystem in isolation from the other subsystems; Table D.5 presents the reuse matrix for the demineralisation plant subsystem operating in combination with the chemical production subsystem; and, Table D.6 presents the reuse matrix for the chemical production subsystem operating in combination with the demineralisation plant subsystem.

From the above listing, Tables D.1, D.2 and D.4 reflect the performance of the subsystems in isolation from each other while Tables D.5 and D.6 reflect the performance of the demineralisation plant subsystem and the chemical production subsystem in combination with each other. The cooling circuit was unaffected by the integration strategy presented in **Chapter 6**; the elements of the chemical production subsystem which were excluded from the optimisation were similarly not affected by the integration strategy. The performance of the various subsystems of the chlor-alkali complex on an integrated basis therefore corresponds to Tables D2 to D6.

Table D.1. *The material reuse matrix derived from the results of the optimisation of the demineralisation plant subsystem in isolation from the other subsystems. The reuse matrix is superimposed on the connectivity matrix of possible matches between sources and sinks for the demineralisation plant subsystem. An unshaded square corresponds to the logical possibility of a connection between a source and a sink. A shaded square corresponds to the impossibility of such a connection. All mass flows are expressed in units of tons.*

Sources \ Sinks	Effluent Treatment Facility	Demineralised Water Storage	Raw Water Demand - Normal Operation	Demineralised Water Demand - Regeneration	Caustic Soda Demand - Regeneration	Hydrochloric Acid Demand - Regeneration	Total flow from Source
Effluent - Cation Regeneration - Pre-Inject & Regenerant Inject Stage	3.2067						3.2067
Effluent - Cation Regeneration - Regenerant Displacement Stage	4.0269					2.7717	6.7986
Effluent - Cation Regeneration - Fast Rinse Stage			3.6421				3.6421
Effluent - Anion Regeneration - Pre-inject & Regenerant Inject Stage	3.2283						3.2283
Effluent - Anion Regeneration - Regenerant Displacement Stage	4.0478				2.7792		6.8270
Effluent - Anion Regeneration - Fast Rinse Stage			3.6421				3.6421
Demineralised Water		241.1814		13.6922			254.8736
Umgeni Water (Municipal Supply)							0
Umbogintwini River Water			254.9337				254.9337
Hydrochloric Acid (31% m/m HCl)						0.3664	0.3664
Caustic Soda (32% m/m NaOH)					0.4077		0.4077
Caustic Soda (38% m/m NaOH)							0
Caustic Soda (50% m/m NaOH)							0
Total Flow to Sink	14.5098	241.1814	262.2178	13.6922	3.1869	3.1381	

Table D.2. *The material reuse matrix derived from the results of the optimisation of the chemical production subsystem in isolation from the other subsystems. The reuse matrix is superimposed on the connectivity matrix of possible matches between sources and sinks for the chemical production subsystem. An unshaded square corresponds to the logical possibility of a connection between a source and a sink. A shaded square corresponds to the impossibility of such a connection. All mass flows are expressed in units of tons per day.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Brine from Electrolyser					1033.8656		
Caustic Soda (32% m/m NaOH)							2.5240
Brine from Primary Dechlorination						1029.2785	
Chlorine Vent from Primary Dechlorination							
Brine from Secondary Dechlorination	49.8838						
Brine from Precipitation							
Brine from Clarification							
Brine Sludge from Clarification	2.6363						
Brine from Primary Filtration							
Brine from Primary Filtration Backwash							
Brine from Secondary Filtration							
Solids Removed from the Brine in Secondary Filtration	0.0082						

cont.

Table D.2. *cont.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Brine from Cation-Exchange Normal Cycle of Operation		1328.0021					
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage							
Effluent - Cation-Exchange Regeneration - Backwash Stage	0.5809						
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage				2.0885			
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage				3.5723			
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage							
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage							
Caustic Soda (38% m/m NaOH) from Caustic Evaporation							
Caustic Soda (50% m/m NaOH) from Caustic Evaporation							
Hydecat Effluent	51.0861						
Hydrogen Chloride Scrubber Effluent							
Demineralised Water			98.6438				
Umbogintwini River Water							
Umgeni Water							

cont.

Table D.2. *cont.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Hydrogen Cooler Condensate							
Hydrogen Chiller Condensate							
Chlorine Cooler Condensate							
Hydrochloric Acid (31% m/m HCl)				6.3400			
Sodium Bisulphite							
Raw Salt							
Sodium Carbonate							
Steam Condensate from Caustic Evaporation							
Process Condensate from Caustic Evaporation							
Pump Seal Water Effluent - Catholyte Pump 1							
Pump Seal Water Effluent - Catholyte Pump 2							
Pump Seal Water Effluent - Filtered Brine Pump 1							
Pump Seal Water Effluent - Filtered Brine Pump 2							
Pump Seal Water Effluent - Polished Brine Pump 1							
Pump Seal Water Effluent - Polished Brine Pump 2							

Table D.2. *cont.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Pump Seal Water Effluent - Anolyte Recovery Pump							
Pump Seal Water Effluent - Backwash Recovery Pump							
Pump Seal Water Effluent - First Effect Circulating Pump							
Pump Seal Water Effluent - Second Effect Circulating Pump							
Pump Seal Water Effluent - First Effect Feed Pump							
Pump Seal Water Effluent - Caustic Soda Product Pump							
Waste Sodium Hypochlorite							
Chlorine Filter Effluent							
Collection Drain							
Steam							
Chlorine Gas							
Total Flow to Sink	104.1952	1328.0021	98.6438	12.0008	1033.8656	1029.2785	2.5240

cont.

Table D.2. *cont.*

Sources \ Sinks	Primary Filtration - Brine Demand	Clarifier - Flocculant - Dilution Demand	Clarifier - Brine Demand	Precipitation - Sodium Carbonate Demand	Precipitation - Caustic Soda Demand	Precipitation - Brine Demand	Secondary Dechlorination - Bisulphite Demand
Brine from Electrolyser							
Caustic Soda (32% m/m NaOH)					0.7152		
Brine from Primary Dechlorination							
Chlorine Vent from Primary Dechlorination							
Brine from Secondary Dechlorination						982.2816	
Brine from Precipitation			1423.2073				
Brine from Clarification	1427.4843						
Brine Sludge from Clarification							
Brine from Primary Filtration							
Brine from Primary Filtration Backwash						100.6855	
Brine from Secondary Filtration							
Solids Removed from the Brine in Secondary Filtration							

Table D.2. *cont.*

Sources \ Sinks	Secondary Dechlorination - Bisulphite Demand	Precipitation - Brine Demand	Precipitation - Caustic Soda Demand	Precipitation - Sodium Carbonate Demand	Clarifier - Brine Demand	Clarifier - Flocculant - Dilution Demand	Primary Filtration - Brine Demand
Brine from Cation-Exchange Normal Cycle of Operation							
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage		5.4779					
Effluent - Cation-Exchange Regeneration - Backwash Stage							
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage							
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage			0.3822				
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage							
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage		1.7641					
Caustic Soda (38% m/m NaOH) from Caustic Evaporation							
Caustic Soda (50% m/m NaOH) from Caustic Evaporation							
Hydecat Effluent							
Hydrogen Chloride Scrubber Effluent			0.2406				
Demineralised Water							
Umbogintwini River Water							
Umgeni Water							

cont.

Table D.2. *cont.*

Sources \ Sinks	Secondary Dechlorination - Bisulphite Demand	Precipitation - Brine Demand	Precipitation - Caustic Soda Demand	Precipitation - Sodium Carbonate Demand	Clarifier - Brine Demand	Clarifier - Flocculant - Dilution Demand	Primary Filtration - Brine Demand
Hydrogen Cooler Condensate		11.0813					
Hydrogen Chiller Condensate							
Chlorine Cooler Condensate							
Hydrochloric Acid (31% m/m HCl)							
Sodium Bisulphite	0.3537						
Raw Salt		142.7128					
Sodium Carbonate				1.0613			
Steam Condensate from Caustic Evaporation		66.3939					
Process Condensate from Caustic Evaporation		79.6573					
Pump Seal Water Effluent - Catholyte Pump 1		3.5842					
Pump Seal Water Effluent - Catholyte Pump 2							
Pump Seal Water Effluent - Filtered Brine Pump 1							
Pump Seal Water Effluent - Filtered Brine Pump 2							
Pump Seal Water Effluent - Polished Brine Pump 1							
Pump Seal Water Effluent - Polished Brine Pump 2		3.5842					

Table D.2. *cont.*

Sources \ Sinks	Secondary Dechlorination - Bisulphite Demand	Precipitation - Brine Demand	Precipitation - Caustic Soda Demand	Precipitation - Sodium Carbonate Demand	Clarifier - Brine Demand	Clarifier - Flocculant - Dilution Demand	Primary Filtration - Brine Demand
Pump Seal Water Effluent - Anolyte Recovery Pump							
Pump Seal Water Effluent - Backwash Recovery Pump							
Pump Seal Water Effluent - First Effect Circulating Pump		0.8387					
Pump Seal Water Effluent - Second Effect Circulating Pump							
Pump Seal Water Effluent - First Effect Feed Pump							
Pump Seal Water Effluent - Caustic Soda Product Pump		0.8387					
Waste Sodium Hypochlorite							
Chlorine Filter Effluent							
Collection Drain		21.9079				6.9133	
Steam							
Chlorine Gas							
Total Flow to Sink	0.3537	1420.8080	1.3380	1.0613	1423.2073	6.9133	1427.4843

Table D.2. *cont.*

Sources \ Sinks	Primary Filtration - Backwash Demand	Secondary Filtration - Brine Demand	Secondary Filtration - Alpha-Cellulose Dilution Demand	Cation-Exchange - Normal Operation Brine Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange Regeneration - Demin Water Demand	Cation-Exchange Regeneration - Hydrochloric Acid Demand
Brine from Electrolyser							
Caustic Soda (32% m/m NaOH)							
Brine from Primary Dechlorination							
Chlorine Vent from Primary Dechlorination							
Brine from Secondary Dechlorination							
Brine from Precipitation							
Brine from Clarification							
Brine Sludge from Clarification							
Brine from Primary Filtration	100.6503	1326.7988					
Brine from Primary Filtration Backwash							
Brine from Secondary Filtration				1327.9990	1.9730		
Solids Removed from the Brine in Secondary Filtration							

cont.

Table D.2. *cont.*

Sources \ Sinks	Primary Filtration - Backwash Demand	Secondary Filtration - Brine Demand	Secondary Filtration - Alpha-Cellulose Dilution Demand	Cation-Exchange Normal Operation - Brine Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange Regeneration - Demin Water Demand	Cation-Exchange Regeneration - Hydrochloric Acid Demand
Brine from Cation-Exchange Normal Cycle of Operation							
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage							
Effluent - Cation-Exchange Regeneration - Backwash Stage						3.8000	0.2294
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage							1.7298
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage							
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage							
Caustic Soda (38% m/m NaOH) from Caustic Evaporation							
Caustic Soda (50% m/m NaOH) from Caustic Evaporation							
Hydecat Effluent							
Hydrogen Chloride Scrubber Effluent							
Demineralised Water							
Umbogintwini River Water							
Umgeni Water							

Table D.2. *cont.*

Sources \ Sinks	Primary Filtration - Backwash Demand	Secondary Filtration - Brine Demand	Secondary Filtration - Alpha-Cellulose - Dilution Demand	Cation-Exchange Normal Operation - Brine Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange Regeneration - Demin Water - Demand	Cation-Exchange Regeneration - Hydrochloric Acid - Demand
Hydrogen Cooler Condensate						8.8785	
Hydrogen Chiller Condensate							
Chlorine Cooler Condensate							
Hydrochloric Acid (31% m/m HCl)							0.3932
Sodium Bisulphite							
Raw Salt							
Sodium Carbonate							
Steam Condensate from Caustic Evaporation							
Process Condensate from Caustic Evaporation							
Pump Seal Water Effluent - Catholyte Pump 1							
Pump Seal Water Effluent - Catholyte Pump 2							
Pump Seal Water Effluent - Filtered Brine Pump 1							
Pump Seal Water Effluent - Filtered Brine Pump 2							
Pump Seal Water Effluent - Polished Brine Pump 1							
Pump Seal Water Effluent - Polished Brine Pump 2							

cont.

Table D.2. *cont.*

Sources \ Sinks	Primary Filtration - Backwash Demand	Secondary Filtration - Brine Demand	Secondary Filtration - Alpha-Cellulose Dilution Demand	Cation-Exchange Normal Operation - Brine Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange Regeneration - Demin Water Demand	Cation-Exchange Regeneration - Hydrochloric Acid Demand
Pump Seal Water Effluent - Anolyte Recovery Pump							
Pump Seal Water Effluent - Backwash Recovery Pump							
Pump Seal Water Effluent - First Effect Circulating Pump							
Pump Seal Water Effluent - Second Effect Circulating Pump							
Pump Seal Water Effluent - First Effect Feed Pump							
Pump Seal Water Effluent - Caustic Soda Product Pump							
Waste Sodium Hypochlorite							
Chlorine Filter Effluent							
Collection Drain			3.1814			7.7384	
Steam							
Chlorine Gas							
Total Flow to Sink	100.6503	1326.7988	3.1814	1327.9990	1.9730	20.4169	2.1230

Table D.2. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda Demand	Caustic Evaporation - 32% m/m NaOH Demand	Caustic Evaporation - 38% m/m NaOH Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Brine from Electrolyser							
Caustic Soda (32% m/m NaOH)		215.9603			62.7897		0.4879
Brine from Primary Dechlorination							
Chlorine Vent from Primary Dechlorination					4.5871		
Brine from Secondary Dechlorination							
Brine from Precipitation							
Brine from Clarification							
Brine Sludge from Clarification							
Brine from Primary Filtration							
Brine from Primary Filtration Backwash							
Brine from Secondary Filtration							
Solids Removed from the Brine in Secondary Filtration							

cont.

Table D.2. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda Demand	Caustic Evaporation - 32% m/m NaOH Demand	Caustic Evaporation - 38% m/m NaOH Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Brine from Cation-Exchange Normal Cycle of Operation							
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage							
Effluent - Cation-Exchange Regeneration - Backwash Stage							
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage							
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage	2.1971				5.2374		
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage	0.0721						
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage							
Caustic Soda (38% m/m NaOH) from Caustic Evaporation			179.3462				
Caustic Soda (50% m/m NaOH) from Caustic Evaporation				136.3031			
Hydecat Effluent							
Hydrogen Chloride Scrubber Effluent							
Demineralised Water							
Umbogintwini River Water							
Umgeni Water							

cont.

Table D.2. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda - Demand	Caustic Evaporation - 32% m/m NaOH - Demand	Caustic Evaporation - 38% m/m NaOH - Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Hydrogen Cooler Condensate							
Hydrogen Chiller Condensate						0.4521	
Chlorine Cooler Condensate					18.9246		
Hydrochloric Acid (31% m/m HCl)							
Sodium Bisulphite							
Raw Salt							
Sodium Carbonate							
Steam Condensate from Caustic Evaporation							
Process Condensate from Caustic Evaporation							
Pump Seal Water Effluent - Catholyte Pump 1							
Pump Seal Water Effluent - Catholyte Pump 2						3.5842	
Pump Seal Water Effluent - Filtered Brine Pump 1						3.5842	
Pump Seal Water Effluent - Filtered Brine Pump 2						3.5842	
Pump Seal Water Effluent - Polished Brine Pump 1						3.5842	
Pump Seal Water Effluent - Polished Brine Pump 2							

cont.

Table D.2. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda Demand	Caustic Evaporation - 32% m/m NaOH Demand	Caustic Evaporation - 38% m/m NaOH Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Pump Seal Water Effluent - Anolyte Recovery Pump						3.5842	
Pump Seal Water Effluent - Backwash Recovery Pump						3.5842	
Pump Seal Water Effluent - First Effect Circulating Pump						2.7454	
Pump Seal Water Effluent - Second Effect Circulating Pump						3.5842	
Pump Seal Water Effluent - First Effect Feed Pump						3.5842	
Pump Seal Water Effluent - Caustic Soda Product Pump						2.7454	
Waste Sodium Hypochlorite						11.6324	
Chlorine Filter Effluent					1.2013		
Collection Drain	0.0351						
Steam						5.2800	
Chlorine Gas					14.7177		
Total Flow to Sink	2.7358	215.9603	179.3462	136.3031	107.4578	51.5287	0.4879

Table D.2. *cont.*

Sources \ Sinks	Hydrogen Chloride Scrubber - Caustic Soda Demand	Total Flow from Source
Brine from Electrolyser		1033.8656
Caustic Soda (32% m/m NaOH)	0.1049	282.7841
Brine from Primary Dechlorination		1029.2785
Chlorine Vent from Primary Dechlorination		4.5871
Brine from Secondary Dechlorination		1032.1654
Brine from Precipitation		1423.2073
Brine from Clarification		1427.4843
Brine Sludge from Clarification		2.6363
Brine from Primary Filtration		1427.4492
Brine from Primary Filtration Backwash		100.6855
Brine from Secondary Filtration		1329.9720
Solids Removed from the Brine in Secondary Filtration		0.0082

cont.

Table D.2. *cont.*

Sources \ Sinks	Hydrogen Chloride Scrubber - Caustic Soda Demand	Total Flow from Source
Brine from Cation-Exchange Normal Cycle of Operation		1328.0021
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage		5.4779
Effluent - Cation-Exchange Regeneration - Backwash Stage		4.6103
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage		2.0885
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage		5.3021
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage	0.1102	2.6895
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage		5.3094
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage		1.7641
Caustic Soda (38% m/m NaOH) from Caustic Evaporation		179.3462
Caustic Soda (50% m/m NaOH) from Caustic Evaporation		136.3031
Hydecat Effluent		51.0861
Hydrogen Chloride Scrubber Effluent	0.1065	0.3471
Demineralised Water		98.6438
Umbogintwini River Water		0
Umgeni Water		0

cont.

Table D.2. *cont.*

Sources \ Sinks	Hydrogen Chloride Scrubber - Caustic Soda Demand	Total Flow from Source
Hydrogen Cooler Condensate		19.9598
Hydrogen Chiller Condensate		0.4521
Chlorine Cooler Condensate	▓	18.9246
Hydrochloric Acid (31% m/m HCl)		6.7332
Sodium Bisulphite		0.3537
Raw Salt		142.7128
Sodium Carbonate		1.0613
Steam Condensate from Caustic Evaporation		66.3939
Process Condensate from Caustic Evaporation		79.6573
Pump Seal Water Effluent - Catholyte Pump 1		3.5842
Pump Seal Water Effluent - Catholyte Pump 2		3.5842
Pump Seal Water Effluent - Filtered Brine Pump 1		3.5842
Pump Seal Water Effluent - Filtered Brine Pump 2		3.5842
Pump Seal Water Effluent - Polished Brine Pump 1		3.5842
Pump Seal Water Effluent - Polished Brine Pump 2		3.5842

cont.

Table D.2. *cont.*

Sources \ Sinks	Hydrogen Chloride Scrubber - *Caustic Soda* Demand	Total Flow from Source
Pump Seal Water Effluent - Anolyte Recovery Pump		3.5842
Pump Seal Water Effluent - Backwash Recovery Pump		3.5842
Pump Seal Water Effluent - First Effect Circulating Pump		3.5842
Pump Seal Water Effluent - Second Effect Circulating Pump		3.5842
Pump Seal Water Effluent - First Effect Feed Pump		3.5842
Pump Seal Water Effluent - Caustic Soda Product Pump		3.5842
Waste Sodium Hypochlorite		11.6324
Chlorine Filter Effluent		1.2013
Collection Drain		39.7762
Steam		5.2800
Chlorine Gas		14.7177
Total Flow to Sink	0.3216	

Table D.3. *The material use matrix for materials not included in the optimisation model for the chemical production subsystem. All flows are expressed in units of tons per day.*

Sources \ Sinks	Effluent Treatment Facility	Desuperheater Demand	Pump Seal Water Demand	Plant Washdown	Drum Pressure Testing	Cylinder Pressure Testing	Hydrochloric Acid Synthesis	Caustic Evaporation - Steam Demand	Clarifier Flocculant - Demand	Secondary Filtration - Alpha-Cellulose Demand	Total flow from Source
Demineralised Water		9.5578	43.0099				39.0867				97.7435
Umbogintwini River Water				3.7701	1.0750	0.4777					5.3227
Steam								66.3939			66.3939
Hydrogen Gas							0.7233				0.7233
Chlorine Gas							18.0514				18.0514
Flocculant									0.0081		0.0081
Alpha-Cellulose										0.0290	0.0290
Plant Washdown Effluent	3.8470										3.8470
Drum Pressure Testing Effluent	1.0752										1.0752
Cylinder Pressure Testing Effluent	0.4780										0.4780
Cylinder Steaming Effluent	0.1150										0.1150
Total Flow to Sink	5.5152	9.5578	43.0099	3.7701	1.0750	0.4777	57.8614	66.3939	0.0081	0.0290	

Table D.4. *The material reuse matrix derived from the results of the optimisation for the cooling circuit subsystem in isolation from the other subsystems. The reuse matrix is superimposed on the connectivity matrix of possible matches between sources and sinks for the cooling circuit subsystem. An unshaded square corresponds to the logical possibility of a connection between a source and a sink. A shaded square corresponds to the impossibility of such a connection. All flows are expressed in units of tons per day.*

Sources \ Sinks	Effluent Treatment Facility	Linde Cooling Circuit Inlet	Sulzer Cooling Circuit Inlet	LC Cooling Circuit Inlet	MBC Cooling Circuit Inlet	Total flow from Source
Umbogintwini River Water		33.2592	75.1972		719.6991	828.1555
Linde Cooling Circuit Outlet		2104.5625	9.7962	211.1046		2325.4633
Sulzer Cooling Circuit Outlet		106.7013	2272.9781			2379.6794
LC Cooling Circuit Outlet	109.6609	113.6145		20894.6008		21117.8762
MBC Cooling Circuit Outlet		31.3025	31.4686	399.2546	19017.0753	19479.1009
Total Flow to Sink	109.6609	2389.4400	2389.4400	21504.9600	19736.7744	

Table D.5. *The material reuse matrix derived from the results of the optimisation of the demineralisation plant subsystem in combination with the chemical production subsystem. The reuse matrix is superimposed on the connectivity matrix of possible matches between sources and sinks for the demineralisation plant subsystem. An unshaded square corresponds to the logical possibility of a connection between a source and a sink. A shaded square corresponds to the impossibility of such a connection. All mass flows are expressed in units of tons per day.*

Sources \ Sinks	Effluent Treatment Facility	Demineralised Water Storage	Raw Water Demand - Normal Operation	Demineralised Water Demand - Regeneration	Caustic Soda Demand - Regeneration	Hydrochloric Acid Demand - Regeneration	Total flow from Source
Effluent - Cation Regeneration - Pre-Inject & Regenerant Inject Stage	2.0634						2.0634
Effluent - Cation Regeneration - Regenerant Displacement Stage	2.5912					1.7834	4.3746
Effluent - Cation Regeneration - Fast Rinse Stage			2.3435				2.3435
Effluent - Anion Regeneration - Pre-inject & Regenerant Inject Stage	2.0773						2.0773
Effluent - Anion Regeneration - Regenerant Displacement Stage	2.6046				1.7883		4.3929
Effluent - Anion Regeneration - Fast Rinse Stage			2.3435				2.3435
Demineralised Water		190.2983		8.8103			199.1086
Umbogintwini River Water			163.7975				163.7975
Umgeni Water							0.0000
Hydrochloric Acid (31% m/m HCl)						0.2358	0.2358
Caustic Soda (32% m/m NaOH)					0.2623		0.2623
Water Exported from the Chemical Production Subsystem			35.3497				35.3497
Total Flow to Sink	9.3365	190.2983	203.8342	8.8103	2.0506	2.0192	

Table D.6. *The material reuse matrix derived from the results of the optimisation of the chemical production subsystem in combination with the demineralisation plant subsystem. The reuse matrix is superimposed on the connectivity matrix of possible matches between sources and sinks for the chemical production subsystem. An unshaded square corresponds to the logical possibility of a connection between a source and a sink. A shaded square corresponds to the impossibility of such a connection. All mass flows are expressed in units of tons per day.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Brine from Electrolyser					1033.8656		
Caustic Soda (32% m/m NaOH)							2.5240
Brine from Primary Dechlorination						1029.2785	
Chlorine Vent from Primary Dechlorination							
Brine from Secondary Dechlorination	49.8838						
Brine from Precipitation							
Brine from Clarification							
Brine Sludge from Clarification	2.6363						
Brine from Primary Filtration							
Brine from Primary Filtration Backwash							
Brine from Secondary Filtration							
Solids Removed from the Brine in Secondary Filtration	0.0082						

cont.

Table D.6. *cont.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Brine from Cation-Exchange Normal Cycle of Operation		1328.0021					
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage							
Effluent - Cation-Exchange Regeneration - Backwash Stage							
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage				2.0885			
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage				3.5723			
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage							
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage							
Caustic Soda (38% m/m NaOH) from Caustic Evaporation							
Caustic Soda (50% m/m NaOH) from Caustic Evaporation							
Hydecat Effluent	51.0861						
Hydrogen Chloride Scrubber Effluent							
Demineralised Water			98.6438				
Umbogintwini River Water							
Umgeni Water							

cont.

Table D.6. *cont.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Hydrogen Cooler Condensate		▨	▨	▨	▨	▨	
Hydrogen Chiller Condensate		▨	▨	▨	▨	▨	
Chlorine Cooler Condensate		▨	▨	▨			▨
Hydrochloric Acid (31% m/m HCl)		▨	▨	6.3400	▨	▨	▨
Sodium Bisulphite		▨	▨	▨	▨	▨	▨
Raw Salt		▨	▨	▨	▨	▨	▨
Sodium Carbonate		▨	▨	▨	▨	▨	▨
Steam Condensate from Caustic Evaporation		▨	▨	▨	▨	▨	▨
Process Condensate from Caustic Evaporation		▨	▨	▨	▨	▨	▨
Pump Seal Water Effluent - Catholyte Pump 1		▨	▨	▨	▨	▨	▨
Pump Seal Water Effluent - Catholyte Pump 2		▨	▨	▨	▨	▨	▨
Pump Seal Water Effluent - Filtered Brine Pump 1		▨	▨	▨	▨	▨	▨
Pump Seal Water Effluent - Filtered Brine Pump 2		▨	▨	▨	▨	▨	▨
Pump Seal Water Effluent - Polished Brine Pump 1		▨	▨	▨	▨	▨	▨
Pump Seal Water Effluent - Polished Brine Pump 2		▨	▨	▨	▨	▨	▨

cont.

Table D.6. *cont.*

Sources \ Sinks	Effluent Treatment Facility	Electrolyser - Brine Demand	Electrolyser - Demineralised Water Demand	Electrolyser - Hydrochloric Acid Demand	Primary Dechlorination - Brine Demand	Secondary Dechlorination - Brine Demand	Secondary Dechlorination - Caustic Soda Demand
Pump Seal Water Effluent - Anolyte Recovery Pump							
Pump Seal Water Effluent - Backwash Recovery Pump							
Pump Seal Water Effluent - First Effect Circulating Pump							
Pump Seal Water Effluent - Second Effect Circulating Pump							
Pump Seal Water Effluent - First Effect Feed Pump							
Pump Seal Water Effluent - Caustic Soda Product Pump							
Waste Sodium Hypochlorite							
Chlorine Filter Effluent							
Collection Drain							
Steam							
Chlorine Gas							
Total Flow to Sink	103.6144	1328.0021	98.6438	12.0008	1033.8656	1029.2785	2.5240

cont.

Table D.6. *cont.*

Sources \ Sinks	Secondary Dechlorination - Bisulphite Demand	Precipitation - Brine Demand	Precipitation - Caustic Soda Demand	Precipitation - Sodium Carbonate Demand	Clarifier - Brine Demand	Clarifier - Flocculant - Dilution Demand	Primary Filtration - Brine Demand
Brine from Electrolyser							
Caustic Soda (32% m/m NaOH)			0.7152				
Brine from Primary Dechlorination							
Chlorine Vent from Primary Dechlorination							
Brine from Secondary Dechlorination		982.2816					
Brine from Precipitation					1423.2073		
Brine from Clarification							1427.4843
Brine Sludge from Clarification							
Brine from Primary Filtration							
Brine from Primary Filtration Backwash		100.6855					
Brine from Secondary Filtration							
Solids Removed from the Brine in Secondary Filtration							

cont.

Table D.6. *cont.*

Sources \ Sinks	Secondary Dechlorination - Bisulphite Demand	Precipitation - Brine Demand	Precipitation - Caustic Soda Demand	Precipitation - Sodium Carbonate Demand	Clarifier - Brine Demand	Clarifier - Flocculant - Dilution Demand	Primary Filtration - Brine Demand
Brine from Cation-Exchange Normal Cycle of Operation							
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage		5.4779					
Effluent - Cation-Exchange Regeneration - Backwash Stage							
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage							
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage			0.3822				
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage							
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage		1.7641					
Caustic Soda (38% m/m NaOH) from Caustic Evaporation							
Caustic Soda (50% m/m NaOH) from Caustic Evaporation							
Hydecat Effluent							
Hydrogen Chloride Scrubber Effluent			0.2406				
Demineralised Water							
Umbogintwini River Water							
Umgeni Water							

cont.

Table D.6. *cont.*

Sources	Secondary Dechlorination - Bisulphite Demand	Precipitation - Brine Demand	Precipitation - Caustic Soda Demand	Precipitation - Sodium Carbonate Demand	Clarifier - Brine Demand	Clarifier - Flocculant - Dilution Demand	Primary Filtration - Brine Demand
Hydrogen Cooler Condensate		0.4566		0.1372			
Hydrogen Chiller Condensate							
Chlorine Cooler Condensate							
Hydrochloric Acid (31% m/m HCl)							
Sodium Bisulphite	0.3537						
Raw Salt		142.7128					
Sodium Carbonate				1.0613			
Steam Condensate from Caustic Evaporation		65.6331					
Process Condensate from Caustic Evaporation		79.7405					
Pump Seal Water Effluent - Catholyte Pump 1		2.4930					
Pump Seal Water Effluent - Catholyte Pump 2		3.5842					
Pump Seal Water Effluent - Filtered Brine Pump 1		3.5842					
Pump Seal Water Effluent - Filtered Brine Pump 2		3.5842					
Pump Seal Water Effluent - Polished Brine Pump 1		3.5842					
Pump Seal Water Effluent - Polished Brine Pump 2		3.5842					

cont.

Table D.6. *cont.*

Sources \ Sinks	Secondary Dechlorination - Bisulphite Demand	Precipitation - Brine Demand	Precipitation - Caustic Soda Demand	Precipitation - Sodium Carbonate Demand	Clarifier - Brine Demand	Clarifier - Flocculant - Dilution Demand	Primary Filtration - Brine Demand
Pump Seal Water Effluent - Anolyte Recovery Pump		3.5842					
Pump Seal Water Effluent - Backwash Recovery Pump		3.5842					
Pump Seal Water Effluent - First Effect Circulating Pump		3.5842					
Pump Seal Water Effluent - Second Effect Circulating Pump		3.5842					
Pump Seal Water Effluent - First Effect Feed Pump		3.5842					
Pump Seal Water Effluent - Caustic Soda Product Pump		3.5842					
Waste Sodium Hypochlorite							
Chlorine Filter Effluent							
Collection Drain						6.9133	
Steam							
Chlorine Gas							
Total Flow to Sink	0.3537	1420.6708	1.3380	1.1985	1423.2073	6.9133	1427.4843

cont.

Table D.6. *cont.*

Sources	Cation-Exchange Regeneration - Hydrochloric Acid Demand	Cation-Exchange Regeneration - Demin Water Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange - Normal Operation Brine Demand	Secondary Filtration - Alpha-Cellulose Dilution Demand	Secondary Filtration - Brine Demand	Primary Filtration - Backwash Demand
Brine from Electrolyser							
Caustic Soda (32% m/m NaOH)							
Brine from Primary Dechlorination							
Chlorine Vent from Primary Dechlorination							
Brine from Secondary Dechlorination							
Brine from Precipitation							
Brine from Clarification							
Brine Sludge from Clarification							
Brine from Primary Filtration						1326.7988	100.6503
Brine from Primary Filtration Backwash							
Brine from Secondary Filtration			1.9730	1327.9990			
Solids Removed from the Brine in Secondary Filtration							

cont.

Table D.6. *cont.*

Sources \ Sinks	Primary Filtration - Backwash Demand	Secondary Filtration - Brine Demand	Secondary Filtration - Alpha-Cellulose Dilution Demand	Cation-Exchange Normal Operation - Brine Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange Regeneration - Demin Water Demand	Cation-Exchange Regeneration - Hydrochloric Acid Demand
Brine from Cation-Exchange Normal Cycle of Operation							
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage							
Effluent - Cation-Exchange Regeneration - Backwash Stage						4.6103	
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage							1.7298
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage							
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage							
Caustic Soda (38% m/m NaOH) from Caustic Evaporation							
Caustic Soda (50% m/m NaOH) from Caustic Evaporation							
Hydecat Effluent							
Hydrogen Chloride Scrubber Effluent							
Demineralised Water							
Umbogintwini River Water							
Umgeni Water							

cont.

Table D.6. *cont.*

Sources \ Sinks	Primary Filtration - Backwash Demand	Secondary Filtration - Brine Demand	Secondary Filtration - Alpha-Cellulose Dilution Demand	Cation-Exchange Regeneration - Normal Operation Brine Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange Regeneration - Demin Water Demand	Cation-Exchange Regeneration - Hydrochloric Acid Demand
Hydrogen Cooler Condensate			3.1814			15.3545	
Hydrogen Chiller Condensate						0.4521	
Chlorine Cooler Condensate							
Hydrochloric Acid (31% m/m HCl)							0.3932
Sodium Bisulphite							
Raw Salt							
Sodium Carbonate							
Steam Condensate from Caustic Evaporation							
Process Condensate from Caustic Evaporation							
Pump Seal Water Effluent - Catholyte Pump 1							
Pump Seal Water Effluent - Catholyte Pump 2							
Pump Seal Water Effluent - Filtered Brine Pump 1							
Pump Seal Water Effluent - Filtered Brine Pump 2							
Pump Seal Water Effluent - Polished Brine Pump 1							
Pump Seal Water Effluent - Polished Brine Pump 2							

Table D.6. *cont.*

Sources \ Sinks	Primary Filtration - Backwash Demand	Secondary Filtration - Brine Demand	Secondary Filtration - Alpha-Cellulose Dilution Demand	Cation-Exchange Normal Operation - Brine Demand	Cation-Exchange Regeneration - Brine Demand	Cation-Exchange Regeneration - Demin Water Demand	Cation-Exchange Regeneration - Hydrochloric Acid Demand
Pump Seal Water Effluent - Anolyte Recovery Pump							
Pump Seal Water Effluent - Backwash Recovery Pump							
Pump Seal Water Effluent - First Effect Circulating Pump							
Pump Seal Water Effluent - Second Effect Circulating Pump							
Pump Seal Water Effluent - First Effect Feed Pump							
Pump Seal Water Effluent - Caustic Soda Product Pump							
Waste Sodium Hypochlorite							
Chlorine Filter Effluent							
Collection Drain							
Steam							
Chlorine Gas							
Total Flow to Sink	100.6503	1326.7988	3.1814	1327.9990	1.9730	20.4169	2.1230

cont.

Table D.6. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda Demand	Caustic Evaporation - 32% m/m NaOH Demand	Caustic Evaporation - 38% m/m NaOH Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Brine from Electrolyser							
Caustic Soda (32% m/m NaOH)	0.2898	216.1859			62.7020		0.2623
Brine from Primary Dechlorination							
Chlorine Vent from Primary Dechlorination					4.5871		
Brine from Secondary Dechlorination							
Brine from Precipitation							
Brine from Clarification							
Brine Sludge from Clarification							
Brine from Primary Filtration							
Brine from Primary Filtration Backwash							
Brine from Secondary Filtration							
Solids Removed from the Brine in Secondary Filtration							

cont.

Table D.6. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda Demand	Caustic Evaporation - 32% m/m NaOH Demand	Caustic Evaporation - 38% m/m NaOH Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Brine from Cation-Exchange Normal Cycle of Operation							
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage							
Effluent - Cation-Exchange Regeneration - Backwash Stage							
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage							
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage							
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage					2.1971		
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage	2.1815				3.1279		
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage							
Caustic Soda (38% m/m NaOH) from Caustic Evaporation			179.5335				
Caustic Soda (50% m/m NaOH) from Caustic Evaporation				136.4455			
Hydecat Effluent							
Hydrogen Chloride Scrubber Effluent							
Demineralised Water							
Umbogintwini River Water						34.6162	
Umgeni Water							

cont.

Table D.6. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda Demand	Caustic Evaporation - 32% m/m NaOH Demand	Caustic Evaporation - 38% m/m NaOH Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Hydrogen Cooler Condensate							
Hydrogen Chiller Condensate							
Chlorine Cooler Condensate					18.9246		
Hydrochloric Acid (31% m/m HCl)							
Sodium Bisulphite							
Raw Salt							
Sodium Carbonate							
Steam Condensate from Caustic Evaporation							
Process Condensate from Caustic Evaporation							
Pump Seal Water Effluent - Catholyte Pump 1							
Pump Seal Water Effluent - Catholyte Pump 2							
Pump Seal Water Effluent - Filtered Brine Pump 1							
Pump Seal Water Effluent - Filtered Brine Pump 2							
Pump Seal Water Effluent - Polished Brine Pump 1							
Pump Seal Water Effluent - Polished Brine Pump 2							

Table D.6. *cont.*

Sources \ Sinks	Cation-Exchange Regeneration - Caustic Soda Demand	Caustic Evaporation - 32% m/m NaOH Demand	Caustic Evaporation - 38% m/m NaOH Demand	Caustic Soda Storage (50% m/m NaOH)	Sodium Hypochlorite Synthesis Demand	Hydecat Destruction Demand	Caustic Soda to Demineralisation Plant
Pump Seal Water Effluent - Anolyte Recovery Pump							
Pump Seal Water Effluent - Backwash Recovery Pump							
Pump Seal Water Effluent - First Effect Circulating Pump							
Pump Seal Water Effluent - Second Effect Circulating Pump							
Pump Seal Water Effluent - First Effect Feed Pump							
Pump Seal Water Effluent - Caustic Soda Product Pump							
Waste Sodium Hypochlorite						11.6324	
Chlorine Filter Effluent					1.2013		
Collection Drain	0.2645						
Steam						5.2800	
Chlorine Gas					14.7177		
Total Flow to Sink	2.7358	216.1859	179.5335	136.4455	107.4578	51.5287	0.2623

Table D.6. *cont.*

Sources \ Sinks	Hydrogen Chloride Scrubber - Caustic Soda Demand	Water Export to Demineralisation Plant Subsystem	Total Flow from Source
Brine from Electrolyser			1033.8656
Caustic Soda (32% m/m NaOH)	0.1049		282.7841
Brine from Primary Dechlorination			1029.2785
Chlorine Vent from Primary Dechlorination			4.5871
Brine from Secondary Dechlorination			1032.1654
Brine from Precipitation			1423.2073
Brine from Clarification			1427.4843
Brine Sludge from Clarification			2.6363
Brine from Primary Filtration			1427.4492
Brine from Primary Filtration Backwash			100.6855
Brine from Secondary Filtration			1329.9720
Solids Removed from the Brine in Secondary Filtration			0.0082

cont.

Table D.6. *cont.*

Sources / Sinks	Hydrogen Chloride Scrubber - Caustic Soda Demand	Water Export to Demineralisation Plant Subsystem	Total Flow from Source
Brine from Cation-Exchange Normal Cycle of Operation			1328.0021
Effluent - Cation-Exchange Regeneration - Brine Displacement Stage			5.4779
Effluent - Cation-Exchange Regeneration - Backwash Stage			4.6103
Effluent - Cation-Exchange Regeneration - Acid Regeneration Stage			2.0885
Effluent - Cation-Exchange Regeneration - Acid Rinse Stage			5.3021
Effluent - Cation-Exchange Regeneration - Caustic Regeneration Stage	0.1102		2.6895
Effluent - Cation-Exchange Regeneration - Caustic Rinse Stage			5.3094
Effluent - Cation-Exchange Regeneration - Brine Replacement Stage			1.7641
Caustic Soda (38% m/m NaOH) from Caustic Evaporation			179.5335
Caustic Soda (50% m/m NaOH) from Caustic Evaporation			136.4455
Hydecat Effluent			51.0861
Hydrogen Chloride Scrubber Effluent	0.1065		0.3471
Demineralised Water			98.6438
Umbogintwini River Water			34.6162
Umgeni Water			0

cont.

Table D.6. *cont.*

Sinks / Sources	Hydrogen Chloride Scrubber - Caustic Soda Demand	Water Export to Demineralisation Plant Subsystem	Total Flow from Source
Hydrogen Cooler Condensate		0.8301	19.9598
Hydrogen Chiller Condensate			0.4521
Chlorine Cooler Condensate			18.9246
Hydrochloric Acid (31% m/m HCl)			6.7332
Sodium Bisulphite			0.3537
Raw Salt			142.7128
Sodium Carbonate		0.8301	1.0613
Steam Condensate from Caustic Evaporation			66.4632
Process Condensate from Caustic Evaporation			79.7405
Pump Seal Water Effluent - Catholyte Pump 1		1.0912	3.5842
Pump Seal Water Effluent - Catholyte Pump 2			3.5842
Pump Seal Water Effluent - Filtered Brine Pump 1			3.5842
Pump Seal Water Effluent - Filtered Brine Pump 2			3.5842
Pump Seal Water Effluent - Polished Brine Pump 1			3.5842
Pump Seal Water Effluent - Polished Brine Pump 2			3.5842

cont.

Table D.6. *cont.*

Sources \ Sinks	Hydrogen Chloride Scrubber - Caustic Soda Demand	Water Export to Demineralisation Plant Subsystem	Total Flow from Source
Pump Seal Water Effluent - Anolyte Recovery Pump			3.5842
Pump Seal Water Effluent - Backwash Recovery Pump			3.5842
Pump Seal Water Effluent - First Effect Circulating Pump			3.5842
Pump Seal Water Effluent - Second Effect Circulating Pump			3.5842
Pump Seal Water Effluent - First Effect Feed Pump			3.5842
Pump Seal Water Effluent - Caustic Soda Product Pump			3.5842
Waste Sodium Hypochlorite			11.6324
Chlorine Filter Effluent			1.2013
Collection Drain		32.5983	39.7762
Steam			5.2800
Chlorine Gas			14.7177
Total Flow to Sink	0.3216	35.3497	