THE APPLICATION OF PINCH ANALYSIS FOR THE RATIONAL MANAGEMENT OF WATER AND EFFLUENT IN AN INDUSTRIAL COMPLEX

CJ Brouckaert · CA Buckley

WRC Report No. 851/1/03

Water Research Commission

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Report to the
WATER RESEARCH COMMISSION

by

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WRC Report No 851/1/03
ISBN No 1-77005-028-0

MAY 2003

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EXECUTIVE SUMMARY

1 Background and Motivation

The damaging effect of the chemical process industry on the environment is one of the greatest challenges facing industry throughout the world. Although industry accounts for only approximately 16 % of the direct water use in South Africa, it often produces effluents, which contain toxins and other damaging pollutants. The damaging effect of industry in South Africa is compounded by a low availability of water. The reduction of both the consumption of water and production of effluent by this economic sector is of vital importance to the protection of South Africa's water resources and environment. The above factors have resulted in wastewater minimisation becoming an important environmental issue to South African industry.

Preventing pollution requires designs that are intrinsically eco-efficient, and not designs that rely on *end-of-pipe* treatment. In order to implement cleaner production designs, the designer requires methods to investigate the implications of the various design possibilities. *Process integration is a holistic approach to process design, retrofitting, and operation which emphasises the unity of a process* (El-Halwagi, 1997).

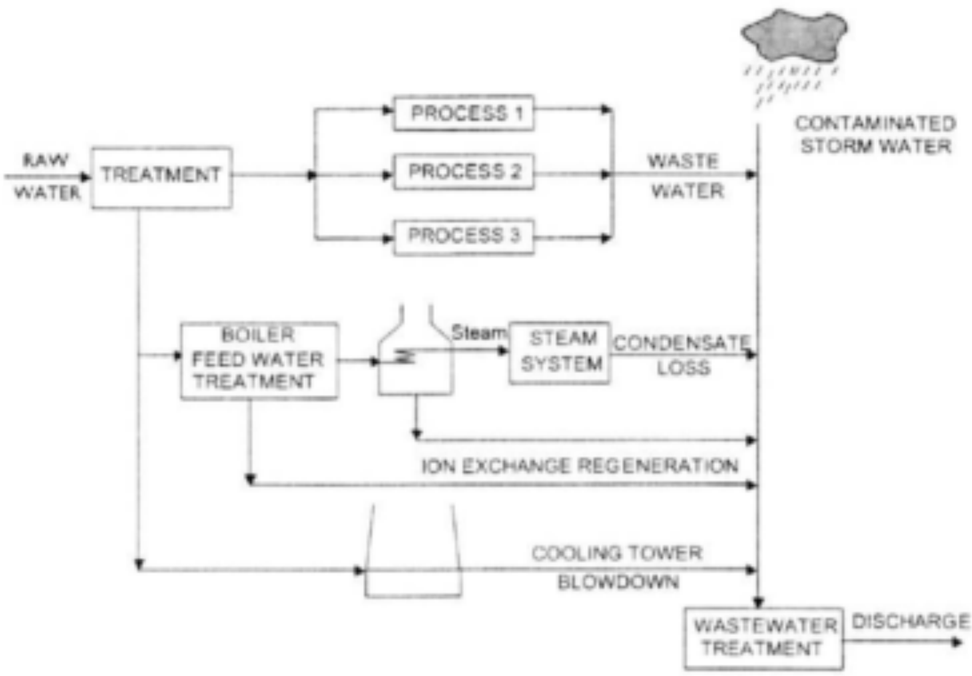

Figure 1: *Typical water use on a chemical process site (Smith, 1995)*

Smith (1995) gave a generalised illustration of water use on a typical process site (Figure 1). Raw water is pre-treated before use in various processes such as washing, (e.g. vessel cleaning). In these processes water comes into contact with process materials, becomes contaminated, and is sent to wastewater treatment. Freshwater (treated raw water) may be upgraded in boiler feed water (BFW) treatment for use in the steam system. Wastewater is generated by ion-exchange regeneration, boiler blow down and condensate loss. Another source of wastewater is the cooling tower blow down. The various wastewater streams are then typically mixed, along with contaminated storm water, and sent to treatment.

Industrial processes thus require water with a range of qualities, and produce a range of effluents, which allow the possibility of a hierarchical use of water.

Possible strategies for reducing the production of wastewater include:

- **reuse:** wastewater from one process can be directly reused in others, provided the level of contamination is sufficiently low to meet the requirements of the subsequent processes;
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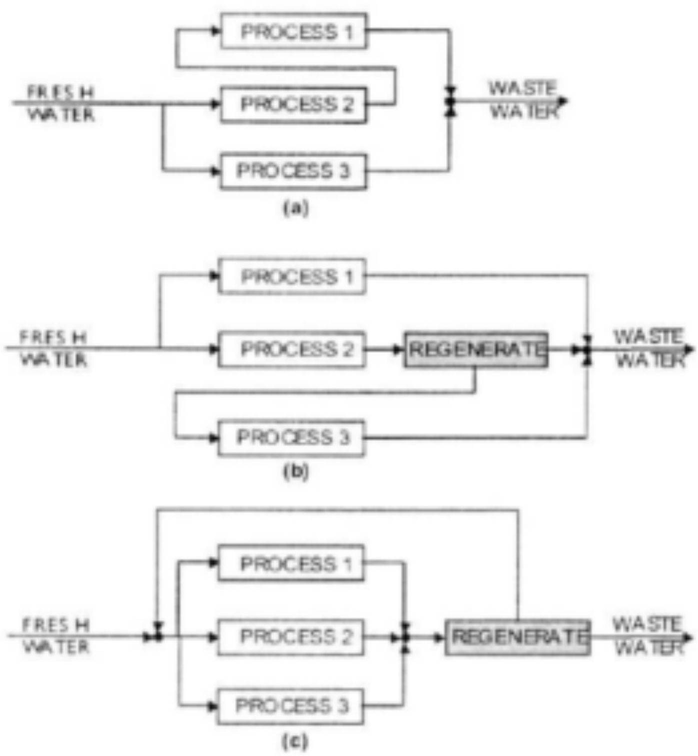

Figure 2: *Water minimisation through (a) reuse, (b) regeneration reuse, and (c) regeneration recycling (Smith, 1995)*

Pinch Analysis is a process integration tool, which was first developed for the design of heat recovery systems during the late 1970s. Using the analogies between heat transfer and mass transfer, a similar approach was developed for the design of mass-exchange systems (El-Halwagi, 1995). This work formed the basis for the design of water-using systems that conform to the usage patterns envisaged by Smith (1995) and illustrated in Figures 1 and 2. It took as the design objective to minimise water consumption by maximising the reuse of water, using a graphical technique (Wang and Smith, 1994a) which was termed *Water Pinch Analysis* (Buehner and Rossiter, 1996). However, the technique was difficult to extend to accommodate the practical constraints and characteristics of water-using systems, such as multiple contaminants, flow rate constraints, piping costs, etc. The added desire to introduce cost optimisation required that the problem be formulated using mathematical programming techniques (Doyle and Smith, 1997).

Water Pinch Analysis thus involves a set of systematic formal techniques to handle the complex problem of hierarchical water allocation to a system consisting of a number of processes, and choosing the best combination of strategies. The theory that appears in the literature is developing rapidly. The practical application of this theory is not well established in the open literature, and particularly not in a South African context.

2 Project Objectives

As originally stated in 1996, the project objectives were:

- To apply and assess the Water Pinch technology and approach for promoting water and effluent conservation in a chemical complex.
- To apply the technique to the AECI Umbogintwini site.
- To make any necessary refinements to the technique.
- To transfer the technology to AECI management, water authorities, consultants and academics.
- To train engineers with the ability to undertake formal water and effluent conservation surveys.

Although the project was originally envisaged as dealing only with factories in the Umbogintwini complex, during the course of the project three other investigations, not associated with the AECI Umbogintwini site, were also initiated. These involved the Sanachem agrochemical factory at Canelands, the Eskom Lethabo Power Station near Vereeniging, and the Mondi Merebank paper mill in Durban.

3 Approach

The AECI Umbogintwini industrial complex, located just south of Durban, consists of 13 individual factories, with site-wide services co-ordinated by a separate company known as AECI Operational Services (AOS). In the original project proposal, it was envisaged that the entire complex would be used as the setting within which to investigate the application of water pinch analysis methods for optimal water and effluent management. This plan, which was not fully realised, would have involved analysing each of the 13 factories in the complex to determine its optimal configuration when seen in isolation from the rest of the complex, followed by an analysis if the whole site, to determine what opportunities exist for optimisation between individual factories.

At the start of the project, in 1997, a preliminary survey identified AECI Bioproducts (lysine), SA Tioxide (titanium dioxide pigment) and Sasol Polymers (chlor-alkali) as the three largest water users in the complex, and these were selected for the initial investigations.

At the same time, the Canelands factory of Sanachem, a subsidiary of Sentrachem, producing agrochemical (principally herbicides and pesticides) requested to join the project. One of their chemical engineers, Thokozani Majozi, was assigned to undertaking the pinch analysis of processes at their site. This work was undertaken as a MScEng project, for which he was allowed to devote 50 % of his time.

Links were established early on to other researchers with interests in pinch analysis, principally Professor Duncan Fraser and Nick Hallale from the University of Cape Town, and Professor Toshko Zhelev from the University of Durban-Westville. A collaborative relationship was also established with the Linnhof-March, the UK consulting firm developing and marketing the WaterTarget™ suite of software for water pinch analysis.

Later in the project, other case studies were initiated as a result of interest from industry. The first of these was a study of the Eskom Lethabo Power Station near Vereeniging, in which the objective was to use pinch analysis to determine the best way to use a reverse osmosis plant within the power station water system. A study of the Mondi Merebank paper mill was started, with a Mondi process engineer, Gladys Naylor (neé Crampton) registering a part-time MScEng student.

Not all of these investigations reached successful conclusions during the course of the project. The initial studies at SA Tioxide and AECI Bioproducts stopped as a result of the resignation of key personnel. Although the AECI Bioproducts investigation was subsequently restarted, it was incomplete at the end of the project period. The Mondi study was also still in progress when the project ended. These incomplete studies, together with a second phase study of the Sasol Polymers plant were carried over into a follow-up WRC project (K5/1158 *The Further Application and Development of Pinch Analysis for Water and Effluent)*.

This left three case studies which yielded significant results during the project period, namely Sasol Polymers, Sanachem and the Lethabo Power Station.

4 Results and Discussion

This section outlines the results obtained at the three sites at which water pinch analysis studies yielded significant results, namely Sasol Polymers, Sanachem and the Lethabo Power Station.

4.1 Sasol Polymers

The initial study was carried out during 1997 by Grant Gardner, and form the basis of his MScEng thesis. At this time we had not fully appreciated the issues of distinguishing between process water streams and utility water streams, nor had we found a systematic way of dealing with multiple contaminants or solutes. The methods found by Gardner to address these problems were very specific to the process in question. The key issue was the presence of hydrochloric acid (HCl) and sodium hydroxide (NaOH) in the system. Essentially, his method divided the plant into two independent subsystems, one for streams and processes containing NaOH, and the other for those containing HCl. These subsystems were then treated as single-contaminant problems, although complications arose due the fact that these were not strictly contaminants, but reagents in the processes. The study identified significant potential savings in the use of water, NaOH and HCl, and in the generation of aqueous effluents, as indicated by the Table 1

The restricted nature of the method did not allow the presence of other contaminants in the system, such as calcium and magnesium, to be taken into account. The results of this study therefore have to be considered as preliminary, and further investigation is required to consider whether these contaminants might preclude any of the suggested reuse options.

Table 1: *Summary of the results obtained from the initial Water Pinch Analysis study carried out at Sasol Polymers*

	Original Flow [kg/h]	New Flow [kg/h]	Percentage Saving [%]
	NaOH Network		
Water	4 785	0	100
Effluent	5 667	1 971	65
NaOH (100% m/m)	1 180	1 146	2.9
	HCl Network		
Water	763	0	100
Effluent	5 467	4 114	25
HCl (31% m/m)	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
NaOH (100% m/m)	1 180	1 146	2.9
HCl (31% m/m)	5 963	5 723	4.2

4.2 Sanachem

The study was aimed at assessing the applicability of WaterPinch principles in water demand reduction, waste minimisation and waste management in general, at Sanachem Canelands. This site contains a number of processes using water as a reaction solvent or a washing solvent for the final products. Consequently, water from these processes is contaminated with salts as well as traces of organic matter (pesticides) from the products. Due to the traces of pesticides, the hazard rating (HR) of most of these streams is quite high which implies that they can only be disposed of in high toxic waste sites, i.e. H:H sites. The streams with low toxicity and high salt content are discharged to the South Durban marine outfall.

Batch processes, unlike continuous processes, are constrained with respect to time and concentration. Water reuse can only be effected subject to these two constraints. This implies that water can be used in another process if, and only if, it is available at the right time and concentration.

A group of processes at the factory were selected for the case study, because they all involved the common "contaminant" NaCl, which is, in fact, reaction by-product in the formation of all the products involved. Bromoxynil octanoate is a herbicide, and fernvalerate and cypermethrin are pyrethrins (insecticides).

During the course of these investigations, an overall reduction of 96 kL/mth of toxic effluent, 216 kL/mth of non-toxic effluent, and an increase of 25 % in production capacity (due to reduced batch times) were identified as a result of the pinch analysis, together with other waste minimisation measures. This represented about 40 % reduction in water use by the processes involved. Unfortunately, before the implementation stage was reached, Sanachem was bought by Dow Chemicals, and the processes in question were closed down as part of an international rationalisation programme.

4.3 Lethabo Power Station

In this investigation, a start was made with formulating an approach to applying the principles of water pinch analysis to the water systems of a power station, with the particular objective of establishing the best use of an existing tubular reverse osmosis (TRO) plant in the system. The study was based on the Eskom Lethabo Power Station located close to the Vaal River near Vereeniging, South Africa. This 3.6 GW plant is built adjacent to the open cast coal mine which supplies its fuel. The main source of water for cooling and for boiler operation is the Vaal River. The station was designed according to a *zero-liquid-effluent* philosophy, in which effluents are concentrated to the point where the residual volume can be accommodated on the coal-ash heaps, where the liquid serves a dust-suppression function. A TRO plant is used to achieve the necessary concentration ratio at times when this cannot be accomplished by evaporation alone: this only occurs occasionally, so the TRO plant does not operate continuously. The associated coal mine is a source of contaminated mine water, most of which was discharged at the time under a permit granted by the Department of Water Affairs, which was to be withdrawn, because of the quite severe problem of salination of the Vaal River.

The standard situation addressed by a pinch analysis calls for minimisation of the total amount of fresh water supplied to the set of processes. The situation under consideration here was more complex, because there was more than one water source (river water and mine water) and because increasing the salt concentration in the feed to the ion exchange increased the use of chemicals for regeneration. Furthermore, the use of mine water in the cooling circuit reduced the evaporation ratio that could be achieved, which ultimately increased the overall effluent discharged from the station, to the point where it could no longer be retained by the ash heaps. This appears to be precluded by Eskom's zero effluent discharge policy, but only if the power station is viewed in isolation from the mine. If they are considered together, it is clear that any mine water that the power station does not accept must be treated separately, or discharged to the environment.

Thus there is a balance that must be struck between use of river water, use of mine water, use of regeneration chemicals, and volume of effluents. This is represented in the pinch analysis as a cost coefficient for each of these factors, which must have values which are in the correct relationship to one another. In principle, these should include a representation of relative environmental costs, not simply financial costs.

The following conclusions were reached about the power station:

Firstly, if the power station is viewed in isolation from the mine, the TRO plant is not required at all; indeed up to about 30 ML/mth of mine water can be used without bringing the TRO plant into play, and without discharging any effluent beyond the capacity of the ash heaps.

Secondly, if the cost of discharging salt is ignored, the low cost of the mine water causes the full quantity available to be used in the cooling circuit, once again without the TRO plant running, however 46 tonnes per month of salt are discharged to the environment.

To address this problem, a cost of discharging salt to the environment had to be established. This was estimated from data provided in WRC Report No. TT 123/00 *The Economic Cost Effects of Salinity*, and represented the cost to the national economy of the salination of the Vaal river.

When this cost was included in the analysis, it forced the TRO plant to be brought into operation, reducing the effluent volume to the ash heap capacity, resulting in no liquid discharge to the environment, which using all the mine water.

From this it was concluded:

- It is technically feasibly to run the mine and the power station together on a zero-liquid-effluent basis, which captures all the saline effluents on the ash heaps, by using the existing TRO plant.
- An incentive is needed to justify this economically. It appears that the magnitude of this required incentive is of the order of the cost to the national economy of salination of the water supply, which should be of interest to regulatory authorities. Eskom is currently sponsoring research to develop a decision-support methodology which can take into account issues like this, which are difficult to quantify in purely techno-economic terms.

5 Conclusions

This project represented a new field for the researchers involved, and the case studies that were undertaken met with a mixture of successes and failures, with some incomplete at the end of the project period. The *Guide to Conduction a Water Pinch Analysis Investigation* presented in **Chapter 3** of the report attempts to summarise the experience gained during these investigations, and is perhaps the chief immediate outcome of the project.

Industrial awareness of the technique in South Africa has been raised through direct interaction with industries involved in the case studies and through conference papers, workshops and courses presented during the project; however this methodology can not yet be considered as an accepted and establish practice.

The following general conclusions can be drawn about the significance of water pinch analysis:

i) A water pinch analysis provides a clear and systematic picture of the water requirements of a system of processes, subject to the constraints imposed by the technology of the processes and the environment in which they operate.

ii) By identifying the factors which limit further reduction in the water requirements, the technique can focus attention on those areas of the process where technological improvements will be most beneficial in improving water efficiency.

iii) By quantifying the impacts of technological and regulatory limits on a process, water pinch analysis has the potential to provide a rational tool for negotiation between an industry, water authorities and other role players.

iv) Currently published water pinch theory is suited to analysing water which is used in a process as a utility; it is less suitable for situations where water is intrinsic to the technology of the process, for example in a hydrometallurgical process.

v) Because South Africa is a water-scarce country, many South African industries have responded to pressure to conserve water, and already have processes which use water relatively efficiently when compared to many industrialised countries. This means that dramatic savings in water use, as sometimes claimed in the international literature, are often not as readily available in South Africa.

vi) There is a need for a technique to provide a rapid assessment of a process to estimate the scope that it offers for improvement as a result of conducting a water pinch analysis.

vii) Gathering the necessary data on a system is almost always the most difficult and most time-consuming step in a water pinch analysis. It is unlikely that all the required data will be obtained at the first attempt, and so an iterative process which alternates between data gathering and analysis occurs.

viii) It is difficult, if not impossible, for an effective pinch investigation to be undertaken by a consultant outside the industrial organisation concerned, unless it is done with the full commitment and participation of the organisation at all stages.

6 Recommendations

i) Further efforts are required to encourage wider acceptance of water pinch analysis by South African industry. This should be undertaken in conjunction with industry on a case study basis.

ii) Further work is needed to extend the water pinch analysis methodology to account for chemically reacting solutes and aqueous reagents.

iii) Techniques for the early identification of the applicability of water pinch need to be developed.

iv) Techniques need to be developed to reduce the time and effort required to gather the data needed for a water pinch analysis.

v) The use of water pinch analysis as a tool for co-regulation should be explored. This will require studies in which regulatory authorities are involved as partners.

vi) Local consultants should be encouraged to set up a water pinch analysis service to industry.

vii) The energy efficiency of a process has a significant impact on its water use for cooling and the concomitant generation of saline effluents. The simultaneous optimisation of water and energy use is therefore an important direction for further investigation.

7 Technology Transfer

Technology transfer to South African industry was an intrinsic part of the motivation for the project, and the case study investigations could be seen as technology transfer exercises for the companies involved. However, specific technology transfer activities went hand in hand with the technical activities. Apart from routine report-back meetings with the companies, a number of presentations and courses on pinch analysis were given at a various meetings and symposia (see list below).

In November 1999 the Process Integration Centre of the University of Manchester Institute of Science and Technology (UMIST), with funding from the British Foreign and Commonwealth Office's *Climate Change Challenge Fund*, led a team which gave a series of presentations to promote Pinch Technology in South Africa. This was the first phase of a project with four phases:

i) awareness building

ii) demonstration (by a water pinch consortium member)

iii) detailed study (by a water pinch consortium member)

iv) Implementation

During the visit, seminars were presented in Cape Town, Secunda, Johannesburg and Durban. The Cape Town seminar was organised by Prof. Duncan Fraser of the University of

Cape Town. Arrangements for the three remaining seminars were handled by the Pollution Research Group at the University of Natal.

The following list summarises the presentations and publications associated with the project:

BUCKLEY, C.A. and BROUCKAERT, C.J., Planning for the Desalination of Mine Water - The Big Picture, *WISA Mine Water Division, Symposium on the Desalination and Management of Saline Effluent in the Middle Vaal Catchment Area*, Western Transvaal Regional Water Co. Recreation Centre, 12 March 1998. (Slide Presentation)

BUCKLEY, C.A., Case Study - Successful Waste Minimisation Programmes in Industry, *Chemical and Allied Industries Association, Responsible Care Workshop*, Airport Garden Court, Gauteng, 11 March 1998. (Talk)

BUCKLEY, C.A., Pinch Analysis as a Technique for Water and Waste Minimisation in Industry - Outline and Examples *Chemical and Allied Industries Association, Responsible Care Workshop*, Breakers Resort, Umhlanga Rocks, Durban, 18 March 1998. (Talk)

BUCKLEY, C.A., Pinch Analysis as a Technique for Water and Waste Minimisation in Industry - Outline and Examples, *Chemical and Allied Industries Association, Responsible Care Workshop*, Sanlam Training Centre, Bellville, Cape Town, 25 March 1998. (Talk)

MAJOZI, T., BROUCKAERT, C.J. and BUCKLEY, C.A., Waterpinch Applied to Batch Processes, *WISA 98 Biennial Conference and Exhibition*, Cape Town, 4-7 May 1998. (poster)

HENRY, P., BROUCKAERT, C.J., and BUCKLEY, C.A., The Application of Pinch Technology as a Strategic Tool in the Rational Management of Water and Effluent in an Industrial Complex, *WISA 98 Biennial Conference and Exhibition*, Cape Town, 4-7 May 1998. (Poster)

MAJOZI T., Water Pinch Analysis, *South African Regional Conference on Cleaner Production*, Eskom Conference Centre, Midrand, 11-13 May 1998 (Course)

BROUCKAERT C.J., Thermal Pinch Analysis, *South African Regional Conference on Cleaner Production*, Eskom Conference Centre, Midrand, 11-13 May 1998 (Course)

MAJOZI, T., BROUCKAERT, C.J. and BUCKLEY, C.A., Effluent Reclamation and Reuse in a Group of Agrochemical Manufacturing Plant Using Process Integration, *Fourth International Symposium on Waste Management Problems in Agro-industries*, Istanbul, Turkey, 23-25 September 1998. (Paper)

BROUCKAERT, C.J., MAJOZI, T., GARDINER, G. and BUCKLEY, C.A., The Application of Pinch Analysis to Water and Effluent Management in the Process Industry, 2nd Asia-Pacific *Cleaner Production Roundtable and Trade Expo, Global Competitiveness Through Cleaner Production*, Brisbane Convention & Exhibition Centre, Brisbane, Australia, 21-24 April 1999. (Paper)

BROUCKAERT, C.J., BUCKLEY, C.A., PETERS, S. and WOODHOUSE, C., Optimal Location of a Membrane Treatment Plant in a Power Station, *International Specialised Conference on Membrane Technology in Environmental Management (IAWQ)*, Tokyo, Japan, 1-4 November 1999. (Paper)

BROUCKAERT, C.J., HANEKOM D., WOODHOUSE, C., and, BUCKLEY, C.A., Optimal Location of a Membrane Treatment Plant in a Power Station, *PowerPlant Chemistry*, **3** (7) 2001

BUCKLEY, C.A., BROUCKAERT, C.J. and RENCKEN, G.E., Waste Water Reuse, The South African Experience, *Water Science & Technology*, **41**(10/11), pp 157-163 July 2000

MAJOZI, T., The Application of Pinch Technology as a Strategic Tool for Rational Management of Water and Effluent in an Agrochemical Industry , *MScEng Thesis*, University of Natal, 1998.

GARDNER, G.A., Liquid Waste Minimisation on a Chloro-alkali Complex, *MScEng Thesis*, University of Natal, 2000.

Finally, pinch analysis was put forward as a key technique in the National Waste Management Strategy, formulated by a task group under the auspices of the Department of Environmental Affairs and Tourism and the Department of Water Affairs and Forestry.

ACKNOWLEDGEMENTS

The research in this report emanated from a project funded by the Water Research Commission and entitled :

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The authors thank the of the Steering Committee responsible for this project for it guidance. Its membership varied during its course; the following persons were members at various times:

Mr GN Steenveld	Water Research Commission (Chairman)
Mrs C Smit	Water Research Commission (Secretary)
Mr FP Marais	Water Research Commission (Secretary)
Dr I Msibi	Water Research Commission
Mr L Gravelet-Blondin	Department of Water Affairs and Forestry
Ms A Rankin	Department of Water Affairs and Forestry
Prof D Fraser	University of Cape Town
Prof T Zhelev	University of Durban-Westville
Prof M Mulholland	University of Natal
Prof BK Loveday	University of Natal
Dr VL Pillay	ML Sultan Technikon
Mr S Ramsuroop	ML Sultan Technikon
Mr D Dyson	AECI
Mr J Singh	AECI
Mr D Gous	Sanachem
Mr B Conlin	Eskom
Mr P Ramlall	Umgeni Water
Mr MJ Pryor	Umgeni Water

The financing of the project by the Water Research Commission and the contribution of the members of the Steering Committee is acknowledged gratefully.

This project was only possible with the co-operation of many individuals and institutions. The authors therefore wish to record their sincere thanks to the following :

Mr R Sayer	Sasol Polymers, Umbogintwini
Mr C Woodhouse	Eskom
Mr D Hanekom	Eskom
Mr A Eastwood	Linnhoff-March
Mr L Govender	AECI Bioproducts

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1 INTRODUCTION

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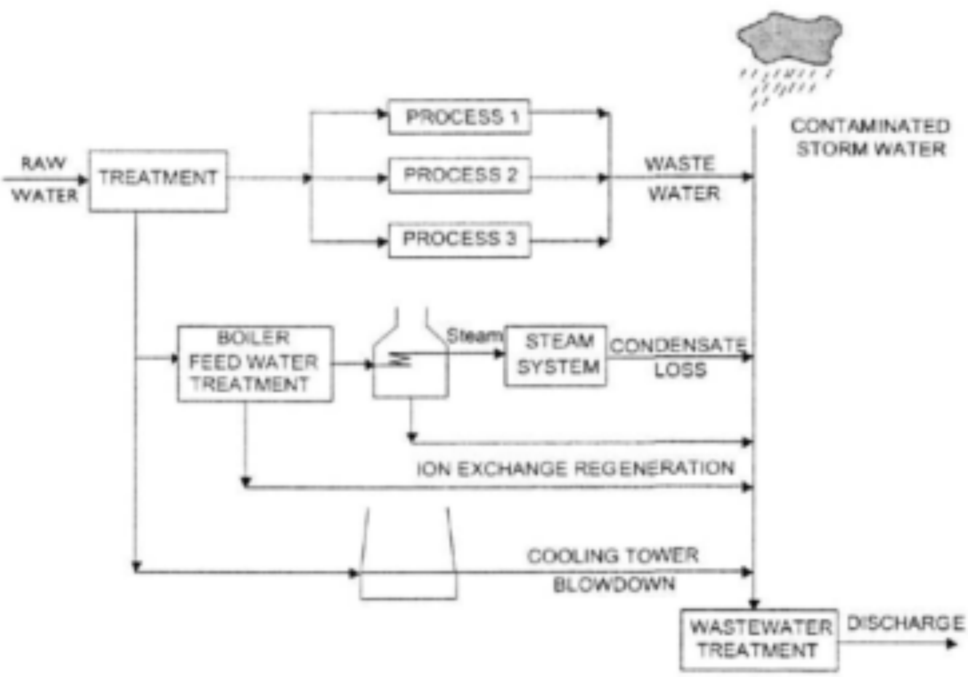

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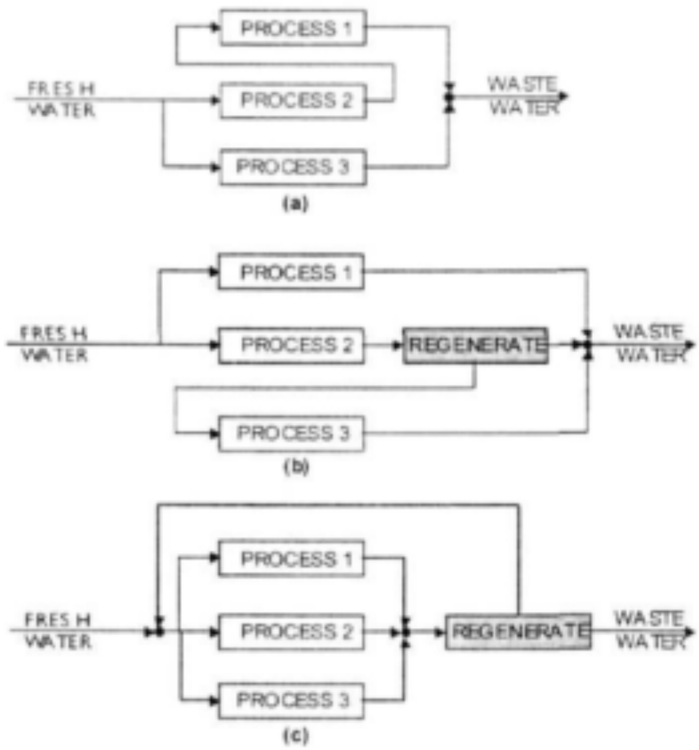

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2 LITERATURE REVIEW

This chapter begins by presenting brief outlines of the literature on the topic from several points of view (**Sections 2.1** to **2.4**), and then review in more detail approaches which were found to be particularly useful for the case studies involved in this project (**Sections 2.5** to **2.7**).

2.1 The Development of Water Pinch Analysis

Preventing pollution requires designs that are intrinsically *eco-efficient* and not designs that rely on end-of-pipe treatment. In order to implement cleaner production designs, the designer requires methods to investigate the implications of the various design possibilities. *Process integration* is a holistic approach to process design, retrofitting, and operation which emphasises the unity of a process (El-Halwagi, 1997). It provides a basis for analysing and developing a design at a relatively early stage of its development by providing global insights of the process to the designer, coupled with methodical targeting and design procedures.

This point of view has lead to the development of process synthesis being defined as *the discrete decision making activities of conjecturing which of the many available component parts one should use, and how they should be interconnected to structure the optimal solution to a design.* (Westerberg, 1987)

Process synthesis systematically guides the designer in the rapid screening of the various process options in order to identify the optimum or near optimum design. It also allows the assessment of the design possibilities before detailed design is initiated.

The first application of these new design techniques involved the conservation of energy through the optimisation of heat exchanger networks. This has led to the development of Pinch Technology as applied to energy conservation. Linnhoff *et al.* (1994) used a graphical approach in which a heat exchange system is represented by a plot of temperature as a function of enthalpy. The streams that require cooling generate the hot composite curve and those that require heating generate the cold composite curve. The cold composite curve is below the hot composite curve. The point at which these curves come in the closest contact is the point at which there is a minimum heat transfer driving force. This point is known as the pinch point. The pinch point is then used to find the minimum process requirement and then the optimal network design. Pinch Technology can also be applied in retrofit situations, however additional restrictive parameters are introduced.

Pinch analysis was initially developed for the optimisation of heat exchanger networks following the methodology proposed by Linnhoff and Flower, 1978. In their paper, the problem of synthesising optimal heat exchanger networks was approached in two successive stages. In the first stage, a preliminary network which yielded maximum energy recovery was generated. This was achieved by splitting the entire problem into ascending temperature intervals and assessing the heat exchange opportunities within each temperature interval. As a result, the entire problem was divided into several sub networks from which the overall heat exchange network was generated. The preliminary network was then used as a starting point for the generation of the most satisfactory networks. This was achieved by the use of a chosen minimum temperature approach (ΔT_{min}) between the hot and the cold streams based on several practical implications. A zero ΔT_{min} set an ideal uppermost bound in energy recovery. The use of the *problem table* in the synthesis of heat exchanger networks was also presented.

Linnhoff, Mason and Wardle (1979) developed this work by applying the proposed methodology to practical problems. The role of ΔT_{min} and the effect of the pinch point in the design of maximum energy recovery networks was further demonstrated. The optimum use of utilities, the determination of the minimum number of process units, the effect of stream splitting and cyclic networks, practical problem constraints as well as data modification were described in detail.

The design method based on the location of the pinch point was described by Linnhoff and Hindmarsh, (1983). This method entailed splitting the problem into two distinct regions, namely the *above pinch* and *below pinch* regions. Targeting for the minimum-utility-use network, with maximum possible energy recovery, was then applied in each of the regions without violating the ΔT_{min} constraint and the necessary criteria around the most constrained region of the overall network, *i.e.* the pinch point. This methodology emphasised the significance of the pinch in heat exchanger network (HEN) design by the introduction of threshold problems. These are problems for which the minimum allowed temperature approach (ΔT_{min}) has no effect on the network design below a certain specified positive value (ΔT_{thresh}).

More recently, the analogies between heat conservation and wastewater minimisation have been used by various people to extend the pinch concept to waste water minimisation. Takama *et al.* (1980) approached the problem of optimal water allocation in a petroleum refinery. In their approach a superstructure of all possible reuse and regeneration opportunities was generated. This superstructure was then optimised and the uneconomical features of the design removed. Takama *et al.* also considered the possibility of regeneration of wastewater. El-Halwagi and Manousiouthakis (1989) adapted the methodology developed by Linnhoff and Hindmarsh (1983) for heat exchanger networks, in order to deal with mass exchange of a single contaminant, between a set of rich process streams and a set of lean process streams. In order to do this they defined a minimum allowable concentration difference that applied throughout the mass exchange network. Since the problem of matching the rich and lean streams is combinatorial they introduced the notion of mass exchange network (MEN) synthesis. This approach was later automated and modified to include regeneration (El-Halwagi, 1990a,b).

In this approach a procedure was developed which allowed the simultaneous synthesis of primary mass exchanger networks and their associated regenerative networks. The regenerative network was aimed at regenerating any recyclable lean streams. The proposed procedure deals with the problem in two stages. The first stage involves the solving of a mixed-integer non-linear programming in order to minimise the cost of mass separating and generating agents. This problem was formulated using thermodynamic constraints. Its solution then allows the location of all the pinch points as well as the optimal flow rates of the lean and regenerative streams. The second stage of the procedure allows the number of units in both networks to be minimised. This is done by solving a mixed integer linear programming problem. El-Halwagi *et al.* (1992) then applied this approach to phenol treatment in petroleum refinery wastewater.

Wang and Smith (1994a) presented a conceptually based approach, in which targets are set that maximise water reuse. Both single and multi-contaminant cases were addressed, along with the identification of regeneration opportunities. Procedures were presented for the design of networks, which allow the minimum target to be achieved. In their methodology different minimum concentration differences can be allowed throughout the network, together with constraints due to corrosion limitations etc. Wang and Smith constructed a composite curve similar to the temperature enthalpy curves introduced in thermal pinch analysis. They then matched this composite curve to a straight line through the origin. This minimum water supply line touches the composite curve at a minimum of two points i.e. the origin and one other. The points other than the origin are known as the Pinch Points. They then presented two methods to achieve this minimum flow rate design. The first is referred to as the maximum driving force method, which uses concentration differences between the various streams to target the minimum flow rate. The second method is referred to as the minimum number of water sources method and uses load intervals. In each interval only enough water is used to maintain network feasibility, the remainder is bypassed and used later. Wang and Smith also considered the case where more than one contaminant is present and extended their methodology to deal with this situation. They also considered the implications of regeneration of wastewater.

In a later paper Wang and Smith (1995a) discussed single and multiple operations with fixed flow rate and processes with multiple sources of water of varying quality. Water loss in processes is also taken into account as well as the possibility of several sources of water of varying quality. New design rules allow novel water flow schemes to be developed based on local recycling and splitting of operations.

Kiperstock and Sharratt (1995) showed that the usual method of incorporating environmental constraints in to a mathematical model as a fixed set of upper limits to concentration for each discharge, is not always the best solution. Better solutions can be obtained by allowing the final discharges to vary in composition, while maintaining a fixed total load.

Dhole *et al.* (1996) introduced an approach slightly different to that of Wang and Smith. This method was designed to overcome the problem encountered in real life application of the Wang and Smith methodology. This methodology was known as the Two Composite Method. Buehner and Rossiter (1996) further expanded this methodology. They used purity on the vertical axis and water flow on the horizontal axis. The input streams of all the water using processes are plotted in a demand composite curve in order to define the water demand for the entire plant. The output streams are plotted in the same way in order to construct the source composite for the entire plant. The composite curves form a pinch point that represents a bottleneck in the reuse of water. The design of the minimum water network is then achieved by the mixing of wastewater of varying qualities in order to relieve the bottleneck in reuse opportunities that is created by the pinch point.

El-Halwagi and Hamad (1996) introduced the concept of synthesising *waste-inception networks* (WINs) and incorporated them into a mass-integration framework for the global allocation of pollutants. This provides a selective inception and re-routing of undesirable species at the heart of the process instead of dealing with the pollutants at the terminal waste streams. It also provides a unified framework for simultaneously tackling gaseous and liquid pollution. This process involves tracking the pollutant through the process and then determining the optimal interception policies. The tracking is done by developing a path diagram as a means of characterising the global flow of the pollutant through the process. The path diagram is then integrated with the interception techniques using mass exchange pinch diagrams. This WIN synthesis strategy is formulated as a mixed integer linear programming problem whose solution yields the optimal interception locations, loads, and separating agents.

Olesen and Polley (1997) reviewed the procedures introduced by Wang and Smith concerning single contaminants. They introduced a new network designing procedure in which they classify operations into distinct types, each of which has distinct design implications. This method is based on the use of a load table, which tabulates the distribution of duties in the region of the pinch and the minimum water needs for each operation. They considered the case of simple reuse, water draws and regenerated water reuse.

El-Halwagi (1997) details some new and interesting techniques developed to handle the problems encountered in real life situations as well as previously developed ideas such as reacting networks (El-Halwagi, 1992) and the combination of thermal and water pinch technology.

2.2 Water Reuse Networks

The hierarchy of methodologies used for the design of water reuse networks is much the same as that for retrofit designs aimed at waste minimisation, these being as follows (Dantus and High, 1996) :

- Hierarchical design procedures
- Pinch technology techniques
- Mathematical programming tools

Hierarchical design procedures consist of a series of heuristic rules, based on engineering knowledge and experience, aimed at screening process alternatives. Their usefulness has its limitations.

Pinch analysis approaches which are graphically based are of limited use when large systems and multiple contaminants are involved. Wang and Smith have developed the methodology for water networks and deal with networks involving multiple contaminants, reuse, regeneration as well as fixed flow rate constraints and multiple water sources (Wang and Smith, 1994a, Doyle and Smith, 1997). The design of water reuse networks which achieve the targeted flow rates is also covered by the theory. Olesen and Polley (1996) extended the methodology to incorporate plant geography and piping constraints. The Two Composite Method (Dhole *et al.*, 1996 ; Beuhner and Rossiter, 1996) is another pinch-analysis-based approach for the design of water reuse networks.

Pinch analysis approaches for the design of distributed effluent treatment plants have been developed by Wang and Smith (1994b), and Kuo and Smith, (1997, 1998a, 1998b). The methodologies are essentially variations of the Wang and Smith methodology.

Doyle and Smith (1997) presented a mathematical programming approach for targeting maximum water reuse in the processing industry. The methodology is based on the concepts developed by Wang and Smith (1994a) in terms of limiting water flows and maximum inlet and outlet concentrations to operations. Where the previous methods could not cope with constraints other than those of concentration and flow rate, the new methodology allows these and others e.g. the ability to forbid matches between operations which might be necessary for geographical or safety reasons.

Although mathematical programming has been used to solve this type of problem previously (Takama *et al.*, 1980 ; Rossiter and Nath, 1995) , the problems considered were small. Doyle and Smith report that the application of these non-linear programming techniques to industrial size problems often produces sub-optimal results due to the method finding local optima rather than the global optima. The approach proposed by Doyle and Smith involves a combined approach of linear and non-linear programming - the linear programming solution is used as an initial estimate for the non-linear programming problem.

Although the case study presented by Doyle and Smith consisted only of *fixed-mass-load operations* (Fig 2.1), the mathematical programming approach may also be applied to operations with more complex contaminant loading models.

Alva-Argaez *et al.*, (1998) extended the work of Doyle and Smith, and incorporated effluent treatment plants in the proposed mathematical programming model. The proposed model includes mass balance constraints, demand and capacity constraints, environmental constraints on waste discharge, design equations for pipes and treatment operation performance constraints.

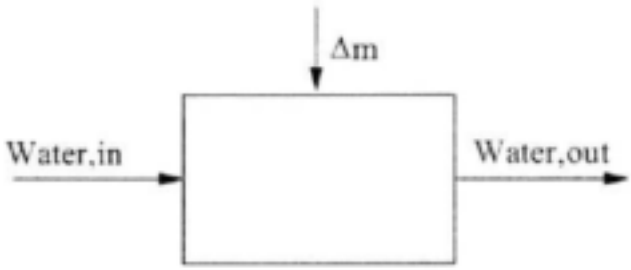


Figure 2.1: *A fixed-mass-load operation*

The state of the art of mathematical programming, as applied to the automated design, integration and operation of chemical processes, has been reviewed by Grossmann *et al.*, (1999).

2.3 Reagent Reuse Networks

While the design of water reuse networks is well documented, no references seem to cover reagent networks. The development of theory covering hydrogen networks has been carried out by Towler *et al.*, (1996). The method presented is graphically based and another form of the Two Composite Method (Dhole *et al.*, 1996 ; Beuhner and Rossiter, 1996). Although formulated for hydrogen, the method is not specific in what material is under consideration and may be extended to reagents. Only the single reagent use is optimised by the method - combined optimisation of water and reagent is not achieved.

2.4 Other Points of Interest

The subject of data extraction and its importance to the final solution achieved by the application of process integration methodologies is dealt with by Linnhoff and Akinradewo (1999). While the context is energy integration based, several aspects are transferable to water-use networks, particularly the consequences of including features of the existing process network as constraints in solving process integration problems.

Dantus and High (1996) used an economic model based on the net present value method which incorporates both manufacturing and capital costs to select the most profitable network configuration in a retrofit design problem. This approach takes into account the time value of money in selecting the best option.

Although written from the perspective of energy integration, Koolen *et al.* (1999) weigh up the vulnerability of integrated chemical complexes to chains of events, leading to total stoppages, against the benefits gained from integration and optimisation. The discussion is directly applicable to water-use networks.

Olesen and Polley (1997) extended Wang and Smith's single contaminant ideas, refining the network design procedures and introduced several new concepts.

Dhole *et al.* (1996) presented a *two composite* method which is closely related to thermal pinch ideas and involves the generation of supply and demand composite curves for the process under consideration. The design method involves mixing of effluents in order to relieve the pinch in the process.

2.5 Single Contaminant, Graphical Approaches to Pinch Analysis

Analogies between heat and mass transfer have been used to extend the concept of pinch analysis to encompass waste minimisation and pollution prevention. Techniques have been developed in order to design optimal mass exchanger networks (MEN). These minimum flow rate networks minimise the amount of fresh water consumed and waste water produced.

El-Halwagi *et al.* (1989-1997) presented several methodologies for the design of MENs, pioneering the extension of the pinch analysis from thermal to mass integration. A brief overview of their work is presented in the first part of this chapter.

Wang and Smith (1994a) developed an approach, which involves the generation of a single composite curve, which is used to set minimum flow rate targets. This approach is presented in the second part of this chapter, closely following their original ideas and examples in order to generate as much conceptual insight as possible into their ideas behind water based pinch analysis. The methods developed allow the designer to identify alternative structures for the same problem. Wang and Smith also considered the possibility of regenerating wastewater and presented a conceptually based approach, which distinguishes between regeneration reuse and regeneration recycling. They later extended this idea to situations where flow rates are constrained (Wang and Smith, 1995a).

2.5.1 El-Halwagi (1989-1997).

The focus of El-Halwagi's work is pollution prevention through source reduction and recycle/reuse but El-Halwagi (1997) concedes that the four waste management activities namely source reduction, recycle/reuse, end-of-pipe-treatment and disposal via post process activities e.g. deep well injection, need to be integrated and reconciled. The most effective design methodology determines the extent to which each of these options should be used. The majority of the theory generated by El-Halwagi and co-workers focuses on the application of process integration for pollution prevention with a large emphasis on mass integration techniques.

El-Halwagi considered the synthesis of optimal mass exchanger networks. Defining a mass exchanger as any direct-contact mass-transfer unit that employs a lean phase (MSA, Mass Separating Agent) to selectively remove certain components from a rich phase. The lean phase should be partially or totally immiscible in the rich phase. The components are redistributed among the phases and this leads to a depletion of the rich phase and an enrichment of the lean phase. The majority of his work concentrates on counter current systems because of their efficiency and industrial importance.

The *mass exchange processes category* includes processes falling into the following categories: liquid-liquid extraction, liquid-gas absorption (scrubbing), liquid-solid absorption, ion exchange, leaching and stripping. Hence examples of mass separating agents (MSAs) are solvents, absorbents etc.

El-Halwagi (1997) described the problem of synthesising Mass Exchanger Networks (MENs) as: given a number N_R of waste (rich) streams (sources) and a number N_S of MSAs, it is desired to synthesise a cost effective network of mass exchangers that can preferentially transfer certain undesirable species from the waste stream to the MSAs.

The target compositions of the undesirable species are assigned by the designer based on the limitations of each application. The MEN synthesis task then attempts to provide the optimal solutions to the following questions.

1) What mass exchange operations should be used?
2) Which MSAs should be used?

3) What is the optimal flow rate of the MSA?

4) How should the MSAs be matched to the waste streams?

5) What is the optimal system configuration?

The designer needs tools that systematically target the optimum solutions to these questions before detailed process design takes place.

El-Halwagi identifies two useful targets, however these targets are normally incompatible. The first of these targets, the minimum cost of the MSAs, involves integrating the thermodynamic constraints of any given problem with the cost data for the individual MSAs. From this it is possible to identify both the minimum cost of the MSAs and the minimum flow rate needed to satisfy any given mass exchange duty.

The second target involves identifying the minimum number of mass exchange units. This is an attempt to minimise the fixed cost of any given network as the cost of a unit is normally a concave function of the unit's size. El-Halwagi and Manousiouthakis (1989) related the number of units to the total number of streams by the following expression.

$$U = N_R + N_S - N_i \qquad (2.1)$$

Here N_i is the number of independent synthesis sub problems, normally one.

Optimisation of the final network design is achieved by trading off the minimum operating cost against the minimum number of units, this is translated as a trade-off between fixed cost (capital outlay) and operating costs (cost of MSAs). Commonly this trade off is achieved by three methods.

In the **first method** the minimum allowable composition difference is used as a trade-off point between the fixed and operating costs (similar to trading off of the minimum temperature difference against network cost in thermal pinch analysis). An increase in the minimum allowable concentration difference results in the increase in the MOC (minimum operating cost) of the network.

The **second method** of achieving this trade-off is the mixing of waste streams. This decreases the number of mass exchangers and hence the fixed cost. However at the same time mixing results in a process MSA or a low cost external MSA becoming infeasible and hence the MOC of the network increases.

The **third method** involves the use of *mass load paths* (El-Halwagi and Monousiouthakis, 1989). This path is a continuous connection that starts with an external MSA and concludes with a process MSA. By shifting the loads along this path, one can add an excess amount of external MSA and remove an equivalent amount of process MSA. These results in the elimination of mass exchangers, but incurs a penalty in the form of increased operating costs. In order to decide whether or not to employ a mass load path, the fixed cost saving achieved by the elimination of mass exchangers should be compared to the additional operating cost incurred.

The first step in *mass integration* is the development of a *global mass allocation* of the whole process from a species viewpoint (El-Halwagi and Hamad, 1996). For each pollutant there are sources (pollutant rich streams) and process sinks (treatment facilities, reactors etc.). Streams leaving the sinks become sources and each sink/generator can be manipulated to affect the flow rate and composition of what each sink can accept and discharge. Effective pollution prevention can be achieved through the combination of a number of concepts (El-Halwagi, 1997), namely *stream segregation, mixing, inception, recycling* and *sink/generator manipulation*.

Segregation refers to avoiding the mixing of streams at the source; this may render some of the streams more environmentally friendly or reduce pollution prevention cost by preventing unnecessary dilution of some streams. It may even provide streams that are sufficiently clean to be directly recycled into a process.

Recycling refers to the utilisation of source streams directly into process units, obviously the constraints of the sink need to be observed. If the constraints of the source are not compatible with those of the sinks, segregation, mixing and/or interception may prepare the sources.

Interception refers to the use of separation units to prepare the sources to make them acceptable to the sinks. These separations are obtained by the use of MSAs and / or ESAs (Energy Separating Agents). Synthesis of MSA induced physical separation is known as mass exchange network synthesis (El-Halwagi, 1997), while the use of reactive MSAs is termed *reactive mass exchange networks* (REAMEN) (El-Halwagi and Srinivas, 1992). Network synthesis techniques for other separation systems such as membrane separation (El-Halwagi, 1992) and *heat-induced separation* (HISEN) (Dunn *et al*, 1995), (Dye *et al.*, 1995) have also been developed.

Sink/generator manipulation uses design or operational changes to alter the composition or flow rate of streams entering or leaving the process units (Crabtree and El-Halwagi, 1995), (Lakshmanan and Biegler, 1995).

El-Halwagi employs several methods in synthesising the MEN, namely graphical, algebraic and mathematical/optimisation programming methods, which are strong analogies of the techniques applied to thermal pinch analysis. For details on mathematical programming approaches the reader is referred to El-Halwagi, (1995).

2.5.2 Wang and Smith (1994-1995)

This series of papers has been very influential in shaping the theory of water pinch analysis.

2.5.2.1 Basic Methodology

According to Wang and Smith (1994a) there are four general approaches to waste minimisation:

1) *Process Changes* - This involves reducing the inherent demand of a process for water.
2) *Reuse* - Waste water can in some cases be reused directly in other operations, provided the level of contamination introduced in the previous operation does not interfere with the process. It may require blending of wastewaters or the blending of wastewater with fresh water.
3) *Regeneration Reuse* - Wastewater can be regenerated by partial treatment to remove contaminants which would prevent its reuse, and then its reuse in other operations. It may not be reused in the operation that generated the waste in the first place, as this recycling will eventually lead to build up within the process. The regenerated water may be blended with other wastewater or with fresh water.
4) *Regeneration Recycling* - Waste water can be regenerated to remove contaminants that have built up, it is then recycled back to the process that generated the waste originally.

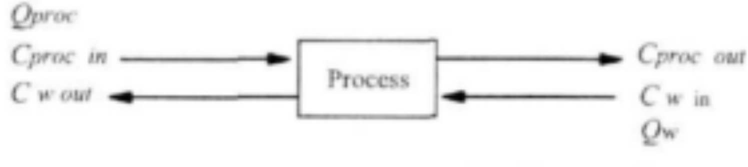


Figure 2.2: *The water-using process considered by Wang and Smith*

Wang and Smith initially considered the water-using process in which a single contaminant is removed from a process stream using water as in Figure 2.2

Different water flow rates and contaminant levels can solve the same problem. In order to maximise the possibility of water reuse from other operations the inlet concentration to a particular operation is set as high as possible, then by specifying the maximum possible outlet concentration, the minimum water flow is defined. This case is known as the limiting case, any water supply line below this (and hence water flow rate above) will satisfy the process requirement. These maximum inlet and outlet concentrations might be fixed by:

1) minimum mass transfer driving force;
2) maximum solubility;
3) corrosion limitations;
4) fouling; etc.

The limiting water profile is used in the analysis because this approach can applied to operations that are very different in nature, and the use of the limiting case allows all the processes to be treated in a standard way.

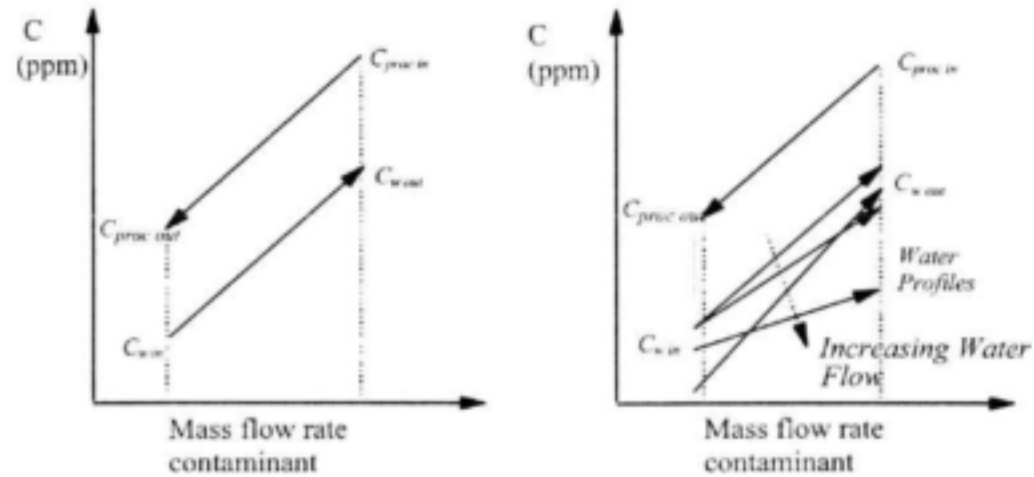


Figure 2.3: *Graphical representation of a process using water to reduce the contaminant level in a process stream - water with different contaminant levels and flow rates can achieve the same effect.*

The Wang and Smith procedure begins with the generation of a table of limiting process water data. This is done for any given process by:

1) Specify the mass load of contaminant (m) to be removed from the process stream.
$$m = Q_{proc}\,(C_{proc\ in} - C_{proc\ out}) \qquad (2.2)$$
2) Specify the maximum allowable contaminant concentration ($C_{w\ in\ max}$) in the feed water or in the outlet ($C_{w\ out\ max}$) determined by process or equipment limitations such as precipitation or corrosion potential.
3) Calculate the maximum concentration of the contaminant in the water outlet stream or in the water inlet.
4) Calculate the minimum wash water flow for each process.
$$Q_w = m\,/\,(C_{w\ out\ max} - C_{w\ in\ max}) \qquad (2.3)$$

This is repeated for each process and the results are tabulated in the format of Table 2.1.

Table 2.1: Limiting process water data (after Wang and Smith (1994a).

Process number	Mass load contaminant (kg/h)	$C_{w\,in\,max}$ (ppm)	$C_{w\,out\,max}$ (ppm)	Water flow (kg/h)
1	2	0	100	20 000
2	5	50	100	100 000
3	30	50	800	40 000
4	4	400	800	10 000

The limiting data presented in Table 2.1 are those given as an example by Wang and Smith (1994a) and are used here to illustrate the single contaminant procedure. For dilute systems mass transfer is assumed to be a linear function of concentration. For concentrated systems each curve can be approximated as a series of linear segments.

The limiting water data are then plotted as *limiting profiles*, Figure 2.4, (note the figures are not to scale). These limiting profiles are then used to construct a *limiting composite curve* (right half of Figure 2.4). Combining the operations within concentration interval generates this composite curve. This curve now represents how the entire system would behave if it was a single water using process and incorporates the process constraints directly.

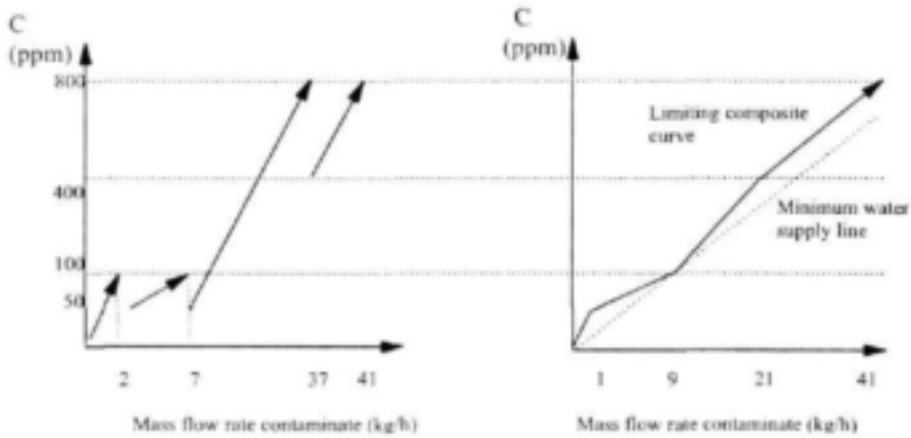


***Figure 2.4:** Limiting water profiles and composite curve for the problem of Table 2.1*

The composite curve shows the critical sections of the plant. These sections are those at or close to the pinch point. These critical sections of the plant require close attention in order to minimise the water flow rate. This composite curve is then matched to a water supply line. The inlet contaminant concentration of the water supply line is assumed to be zero and hence the water supply line will always pass through the origin.

Any line through the origin below the composite curve represents a water supply flow rate that will satisfy the system. The minimum water supply line, representing the minimum water flow rate, is the line that which just touches the composite curve. Each point where the supply line touches the limiting profile creates a pinch in the design. There will generally be at least one pinch point. The inverse of the gradient of this water supply line then specifies the target for the minimum water flow rate.

It is important to note that at the pinch point the case of zero mass transfer driving force does not occur. This is because minimum mass transfer driving forces have already been built into the limiting data.

Having specified the minimum water flow rate, Wang and Smith then present two methods for the network design. The first method maximises the concentration driving forces in the resulting design and takes full advantage of the concentration difference between the limiting composite curve and the water supply line. The strategy involves dividing the limiting composite curve into vertical mass load intervals at each point where the gradient changes (Figure 2.5). Wang and Smith then use the grid diagram (lower part of Figure 2.5) for network design that is a concept initially developed by Linnhoff and Flower (1978).

The generation of the optimum network starts with fresh water in interval 1. In this interval only Process 1 exists and it is matched with fresh water. The water has now reached 11.1 ppm as defined by the water supply line. In interval 2 the water from the exit of interval 1, is now be split between Process 1, Process 2 and Process 3. In the next interval only Process 3 exists and the outlets of Process 1, Process 2 and Process 3 (having reached the pinch concentration) are mixed and passed on to Process 3 as a feed. In the final interval both Process 3 and Process 4 exist and the outlet from interval 3 is split between these processes.

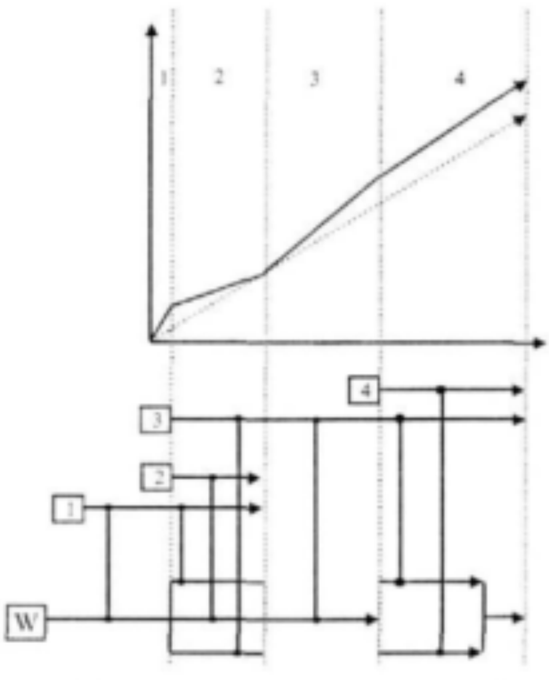


Figure 2.5: *Division of the composite curve into mass-load intervals, and grid diagram for the water-use network design specified in Table 2.1*

While this produces a design (Figure 2.6) which meets the minimum water flow rate, it also leads to unnecessary complexity. Wang and Smith solved this problem by identifying independent loops in the design (Figure 2.7) and then breaking them (Figure 2.8). This leads to a far less complex design that still uses the minimum water. This procedure is analogous to that introduced by Linnhoff and Hindmarsh (1983), used in energy relaxation techniques for the simplification of heat exchanger networks.

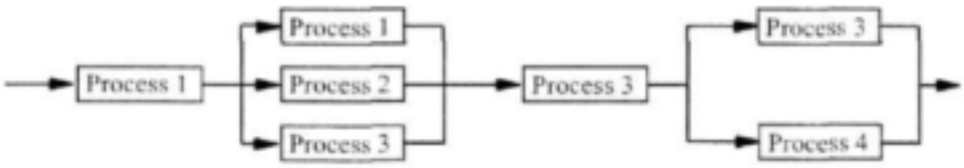


Figure 2.6: *Resulting network design for problem defined in Table 2.1*

In regions far away from the pinch point the driving forces between the composite curve and the water supply line are large and it is possible to break loops in the design without incurring a penalty in the form of an increased water flow rate. Breaking loops around the pinch does, however introduce a increased use of water.

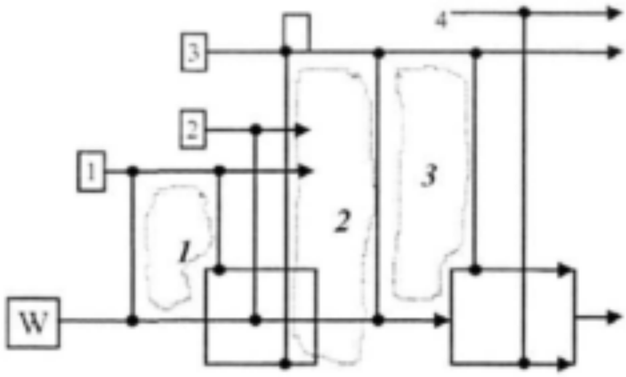


Figure 2.7: *Identification of independent loops in the network design generated by Wang and Smith's maximum driving force method.*

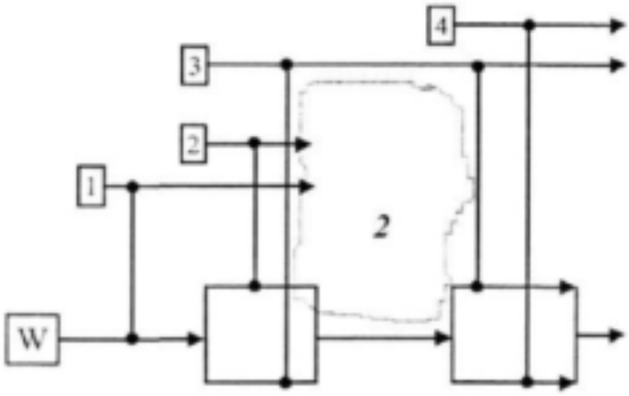


Figure 2.8: *Simplified network design with independent loops broken, generated by Wang and Smith's maximum driving force method.*

The second method introduced by Wang and Smith ensures the minimum numbers of water sources are used. This second method involves following concentration intervals instead of mass load intervals (Figure 2.9)

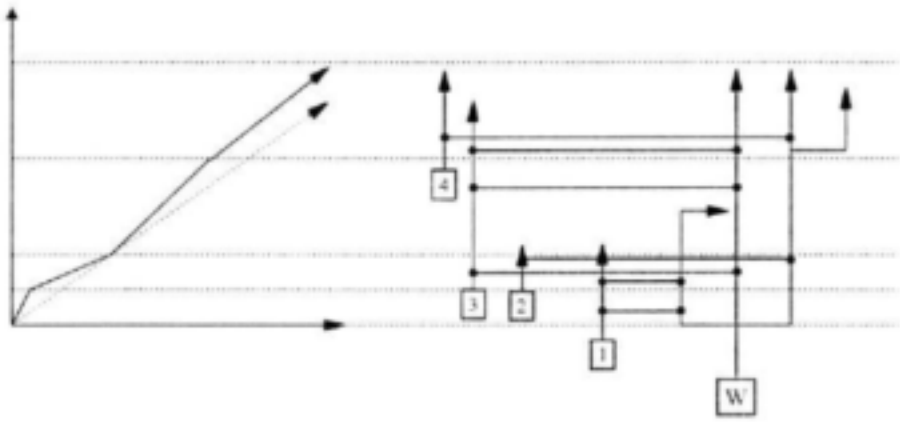


Figure 2.9: *Network design according to the minimum water sources method - the composite curve is divided into concentration intervals.*

In each match only sufficient water is used to maintain network feasibility i.e. the minimum amount of water required by the process is used; the unused water is bypassed to be mixed in later. The design procedure then follows that of the first method including identification and breaking of loops in the initial design. This design strategy combines the minimum flow rate and network simplicity by exploiting bypassing and mixing. It produces a design with only a single water source that still achieves the minimum flow rate target.

2.5.2.2 Regeneration Reuse

Wang and Smith (1994a) consider first the placement of regeneration processes for a single contaminant when reuse but not recycling is allowed. Figure 2.10 shows a limiting composite curve with a water supply line matched against it. The water supply line also shows a regeneration process. In Figure 2.10, the water is taken to concentration C_{Regen} to the limiting composite curve. It then enters a regeneration process, which brings the level of contaminant down to a concentration C_o.

The mass transfer is completed with regenerated water. In Figure 2.10 they assume that the flow rate of water before and after regeneration is the same hence, the water supply lines before and after regeneration have the same slope. If there is a significant change in flow rate before and after regeneration, the construction is easily modified to take this into account by relating the slopes to its flow rate characteristics.

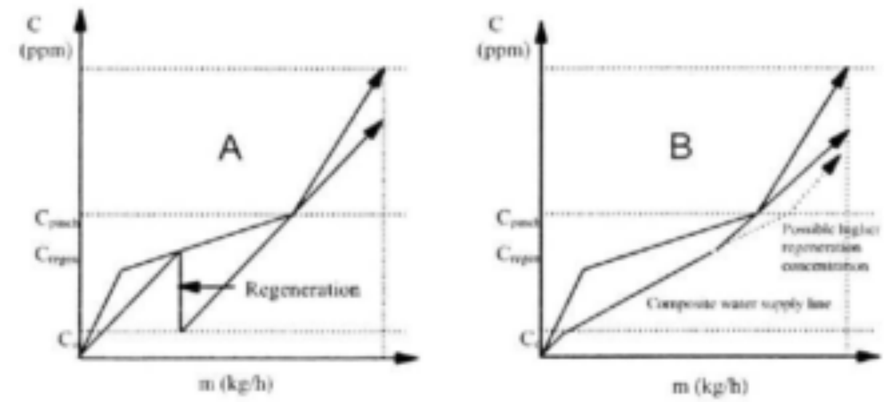


Figure 2.10: *Placement of a water regeneration process relative to pinch*

The placement of the regeneration process as shown in Figure 2.10A clearly brings a reduction in flow rate. To determine whether the flow rate is minimised it is necessary to create a composite of the water supply lines before and after regeneration and match this against the limiting composite curve as shown in Figure 2.10B.

The composite water supply line in Figure 2.10B just touches the limiting composite curve, which seems to indicate that the water flow rate with regeneration is minimised. However, the dotted line shows what would have happened if the water had been allowed to reach a higher concentration before entering the regeneration, there is clearly a gap between this line and the composite curve indicating that the water flow rate is not minimised.

Figure 2.11 shows the same limiting composite curve from Figure 2.10A, but with the water having been allowed to reach pinch concentration C_{pinch} before entering the regeneration process. The outlet of the regeneration process is specified (C_o) and the flow rate before and after regeneration is unchanged. This seems to be infeasible, since the water supply line crosses the limiting composite curve. Once again feasibility can only be determined by creating a composite of the water supply lines before and after regeneration. This is shown in Figure 2.11. The placement with regeneration at pinch concentration is seen to be feasible and the water flow rate is minimised.

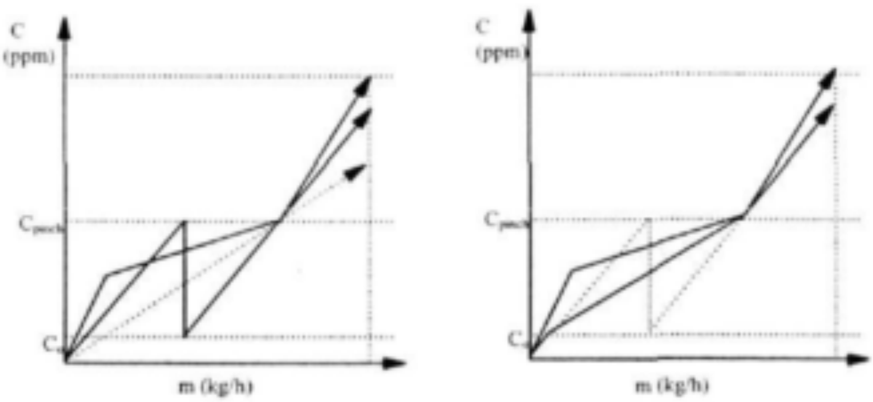


***Figure 2.11:** Placement of a water regeneration process to minimise water flow rate.*

By allowing the water supply line to achieve pinch concentration before regeneration allows the designer to achieve both the minimum water flow rate and the minimum concentration reduction in the regeneration process. A simple mass balance calculates the water supply flow rate:

$$f_{ws} = \frac{m_{pinch} - f_{ws} \cdot C_{pinch}}{C_{pinch} - C_o} \quad (2.4)$$

Returning to the first example used to illustrate the single contaminant approach and applying regeneration with a unit capable of reducing the contaminant level to 5 ppm. The minimum water flow rate (Equation 2.4) is 46.2 t/h. To design with regeneration the same design procedures are used as before, however above the pinch only regenerated water must be used. Below the pinch both regenerated and unregenerated water can be used.

Figure 2.12 shows an initial design based on design method 2 to achieve the target minimum flow rate.

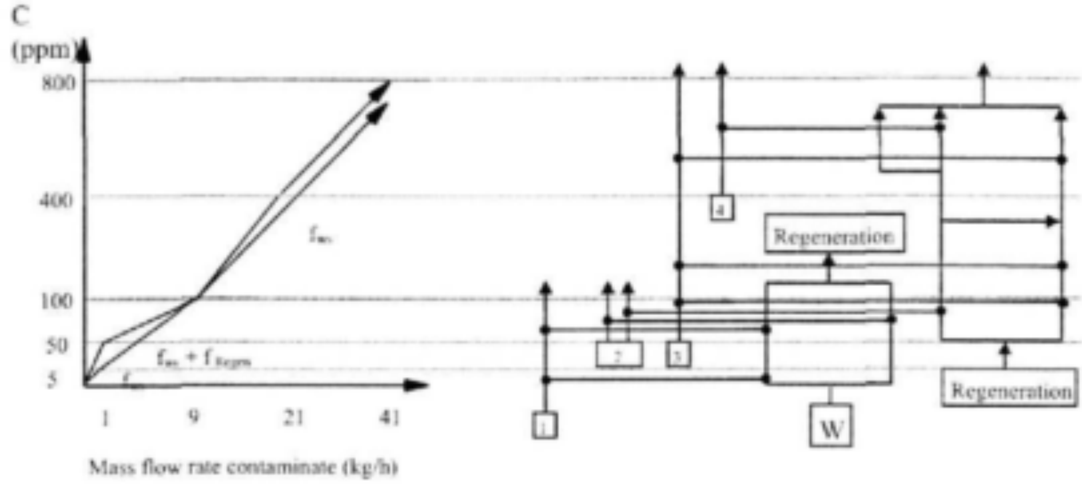


Figure 2.12: *Network design for minimum water use with regeneration.*

Figure 2.13 shows the design with regeneration after the breaking of loops. Although process 2 is contacted with water before and after regeneration, there is no recycle. Different parts of process 2 are serviced by different sources of water.

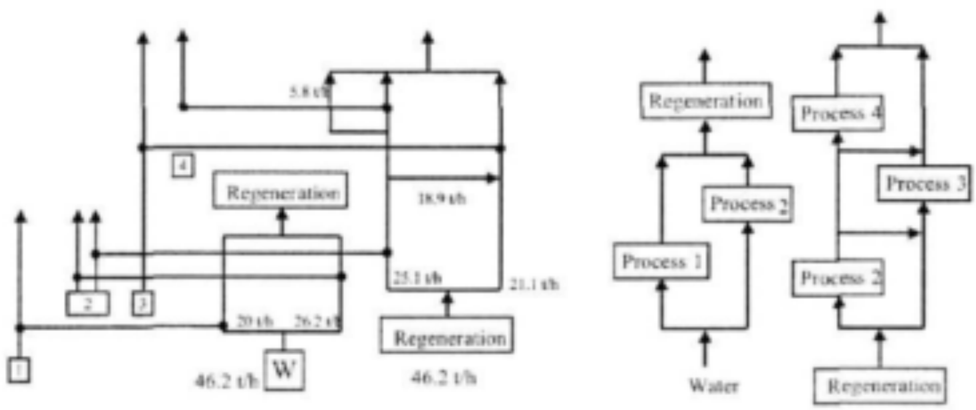


Figure 2.13: *Final Network design for minimum water use with regeneration.*

Situations can arise in which partial regeneration of water is called for. In these situations the slope before regeneration (f_{ws}) is equal to that after regeneration (f_{regen}), indicating total water regeneration. The process cannot support a lower flow rate before regeneration but can support a lower flow rate after regeneration. The unregenerated water with flow rate (f_{ws} - f_{regen}) is also available above the pinch concentration. A simple mass balance gives the regenerated water flow rate:

$$f_{regen} = \frac{m_{pinch} - f_{ws} \cdot C_{pinch}}{C_{pinch} - C_o} \quad (2.5)$$

It is possible to apply the principles developed for regeneration with a specified outlet concentration to a regeneration process defined by removal ratio.

2.5.2.3 Regeneration Recycling

If recycling is allowed, it is possible to reduce the supply flow rate below that for reuse only, with the flow rate reduced to that dictated by the slope of the limiting composite curve below C_o as in Figure 2.14. If this flow rate is allowed to reach C_{pinch} and regenerated as shown in

Figure 2.15 then there is insufficient water to satisfy the problem. The flow rate needs to be increased after regeneration by recycling. In this figure, the slope of the water supply line after regeneration indicates the total flow rate of regenerated water. Figure 2.16 shows a composite curve of the water supply line before and after regeneration.

Applying this approach to the single contaminant example, the new target flow rate of freshwater and wastewater is 20 t/h for regeneration recycling as opposed to 46.2 t/h for regeneration reuse. The target regeneration flow rate is 73.7 t/h. Figure 2.17 shows the new design after loop breaking.

This is an interesting concept, but does not apply when the exit stream from the process is not available for recycling i.e. the exit stream now appears in a final product, or when the 'contaminant' is a desirable species. In such a case, any regeneration is actually destruction of a final product or a valuable reagent. This has some serious implications for almost all the procedures that are available, especially when applied to a real industrial case, since this introduces a further set of considerations to the problem.

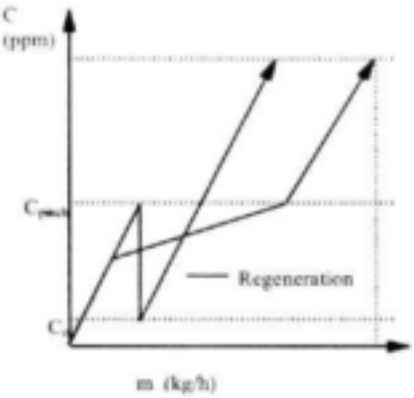


Figure 2.14: *Slope of composite curve below C_o sets the minimum water flow rate.*

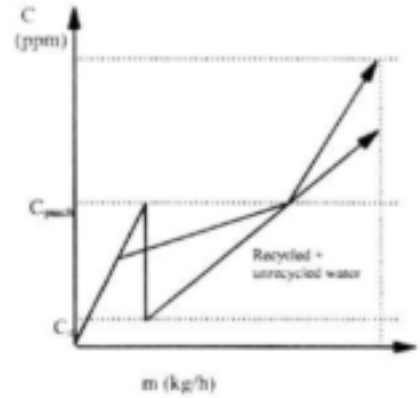


Figure 2.15: *Water supply does not satisfy the problem and an increase in flow rate is required implying recycling is necessary.*

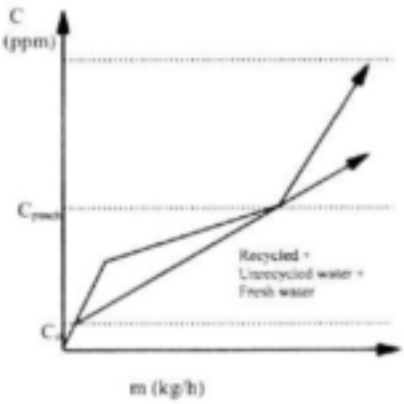


Figure 2.16: *Composite water supply line after regeneration and including recycling.*

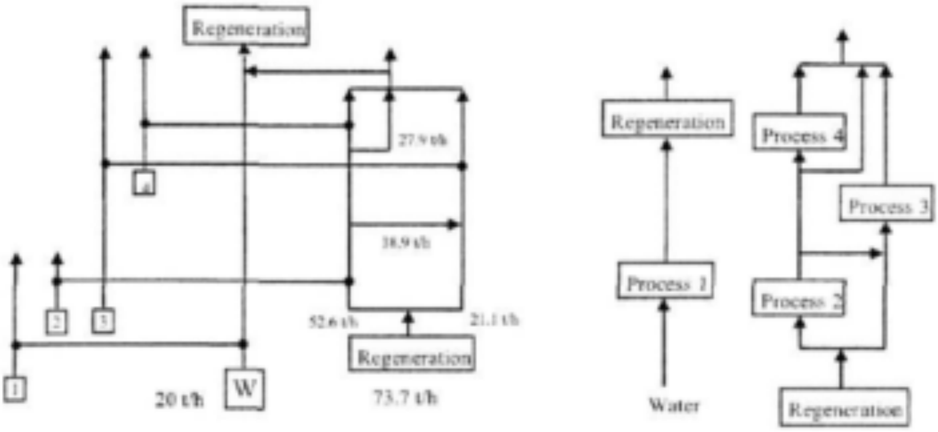


Figure 2.17: Final design with regeneration, after breaking loops.

2.5.2.4 Single Operations with Fixed Flow Rates

Wang and Smith (1995a) investigated single operations with fixed flow rates and the use of pinch technology to minimise this flow. Consider an operation with a maximum inlet concentration of $C_{in\ max}$ and a maximum outlet concentration of $C_{out\ max}$ and the water flow rate fixed at f_L (Figure 2.18).

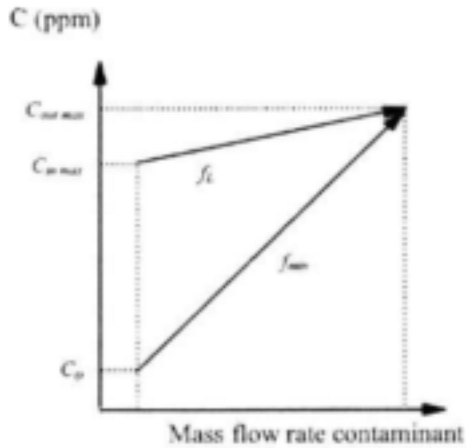


Figure 2.18: Minimum water flow rate for a single process with a fixed flow rate.

It is possible that during the construction of the water supply line that the minimum water flow rate suggested is lower than the required flow rate for the process. This may suggest that this minimum flow rate is now infeasible. However the solution to this problem is relatively simple and takes the form of local recycling around the offending operation. A simple mass balance proves that the inlet concentration to the process is within the limit.

Consider now how this operation illustrated in Figure 2.18 can be designed using f_{min} but without local recycling, and exploiting reuse only. Figures 2.19 and 2.20 illustrate a method of designing for reuse with f_{min} but maintaining the flow rate constraint.

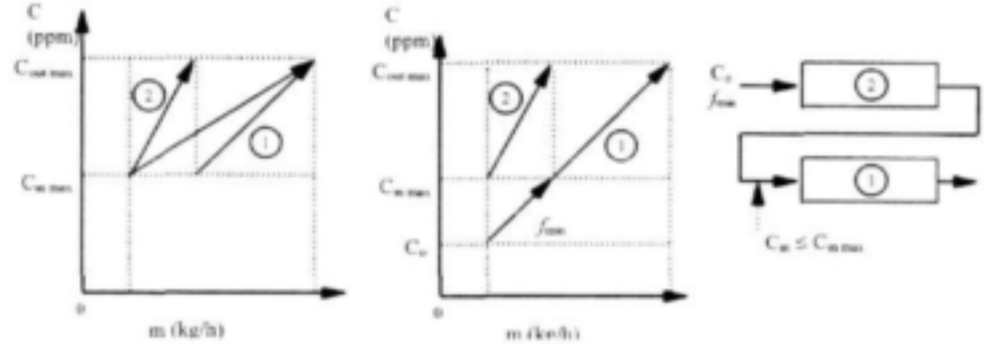


Figure 2.19: *Split operation with part 1 taking f_{min} a feasible design with the lower flow rate fed first.*

In Figure 2.19 the operation has been split into two parts. Whether or not an operation can be split into parts depends very much on the nature of the operation. For example, a multistage washing operation can be readily split, whereas a steam stripping cannot be. In Figure 2.19 the operation has been split such that each part has a flow rate requirement which is less than or equal to f_{min}. Here part 1 of the operation has been taken to have a flow rate equal to f_{min}, part 2 taking the remainder of the flow rate. Figure 2.19 shows that if water is reused between these two parts, the design will be feasible if the part requiring the lower flow rate is fed first. On the other hand, Figure 2.20 shows the same split but in a different order. If water is reused between the two parts, with the part requiring the larger flow rate being fed first, the outlet concentration from part 1 exceeds the maximum inlet concentration for part 2 and the design is infeasible.

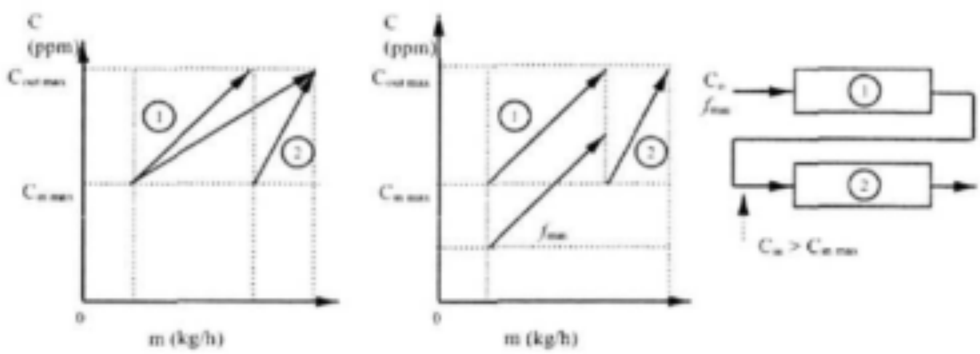


Figure 2.20: *Split operation with part 1 taking f_{min}, but used in a different order to that in Figure 2.19 - reuse with the larger part being fed first leads to an infeasible design.*

2.5.2.5 Multiple Operations with Fixed Flow Rates.

Consider now the limiting composite curve in Figure 2.21, in which all of the operations, which comprise the composite curve, have a fixed flow rate. A water supply line has been matched against the limiting composite curve. The construction has also been split into vertical mass load intervals.

In mass load intervals II and I the total flow rate requirements exceed f_{min}. This implies that the straightforward design method will produce an infeasible design.

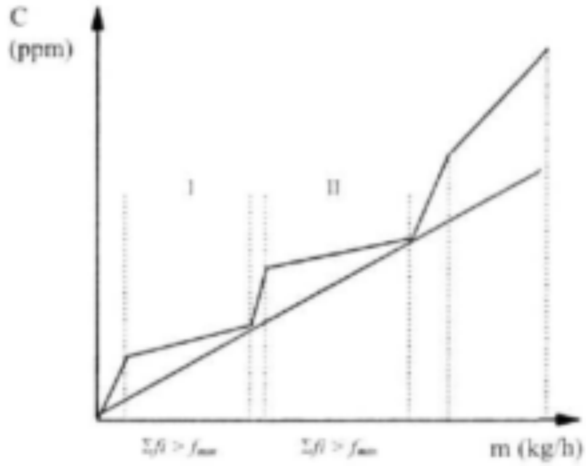


Figure 2.21: *Composite curve of several fixed-flow-rate processes, flow rates in some of the mass load intervals are larger than the minimum flow rate.*

Of the two intervals, interval II, leading up to the pinch, is the most constrained. Consider this interval in more detail. The only difference in principle between the single process in Figure 2.18 and interval II in Figure 2.21 is that the stream in interval II comprises several streams. It is therefore always possible to design for this interval using local recycling. The outlets from the individual operations may be mixed before local recycling takes place.

If local recycling is not acceptable it is possible to design using the philosophy adopted for reuse with single operations. The difference now is that the operation is naturally split since the overall system already consists of several operations. As long as each operation requires a flow rate less than or equal to fmin there is no need to split individual operations. If needs be individual processes can be split into parts satisfying the constraint that each operation or part-operation should require a flow rate less than or equal to fmin. The order of reuse must also be in increasing order of flow rate requirement. A simple mass balance can demonstrate the feasibility of the design.

If local recycling is not desirable and operations cannot be split, then the target for each interval can no longer be f_{min}. Since each operation for reuse must have a flow rate requirement less than or equal to f_{min} for reuse, if operation splitting is not allowed for the interval then the target flow rate f_T given by:

$$f_T = \text{Max}\{ f_{min}, f_i \} \qquad (2.6)$$

Where the steepest water supply line gives f_{min}, which can be matches against the limiting composite curve and f_{min} are the flow rate requirements for the individual operations. Note that equation 2.6 only guarantees that operation splitting within any individual interval is not necessary. It might still be necessary to split an operation between intervals.

Wang and Smith (1995a) combined the insights gained in their first paper (1994a) with their ideas on splitting operations and local recycling and presented a design method, which produced minimum flow rate designs. This design method closely follows that presented in the previous paper, but satisfies flow rate constraints by one of the methods discussed above.

To adapt the approach above for single contaminants to the placement of regeneration processes with multiple contaminants, a reference contaminant is chosen, and the limiting composite curve is constructed based on that contaminant (using shifting where necessary).

2.5.2.6 Multiple Sources of Fresh Water.

Consider a situation where there are three sources of freshwater available, demineralised water, potable water and bore hole water. The highest quality is demineralised water and the lowest purity is bore hole water. Figure 2.22 shows a limiting composite curve using only high quality freshwater with no contamination. Potable water is available with a concentration of contaminant C_{POT}.

In Figure 2.23 demineralised water is substituted by potable water above C_{POT}. The slope of the limiting composite curve below dictates the minimum amount of demineralised water which is necessary. The difference in slope between the water supply line below and above C_{POT} dictates the amount of potable water. In Figure 2.24 part of the water is now substituted by bore hole water above concentration C_{BH}. This construction now maximises the use of low quality water.

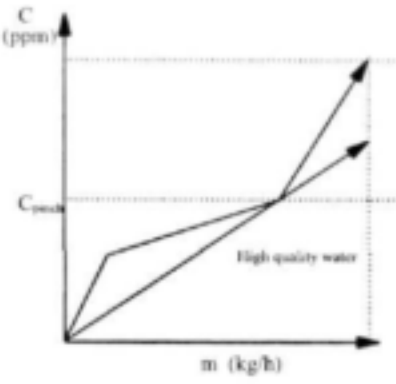


***Figure 2.22** : Targetting minimum flow rate using only high quality water.*

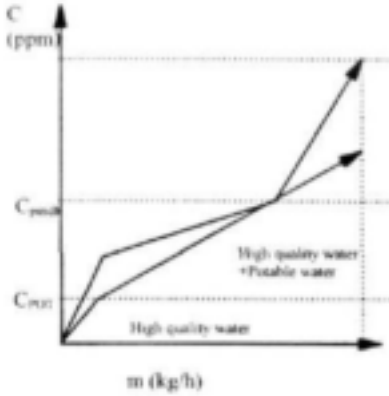


***Figure 2.23** : Targetting minimum flow rate using high quality and intermediate quality water.*

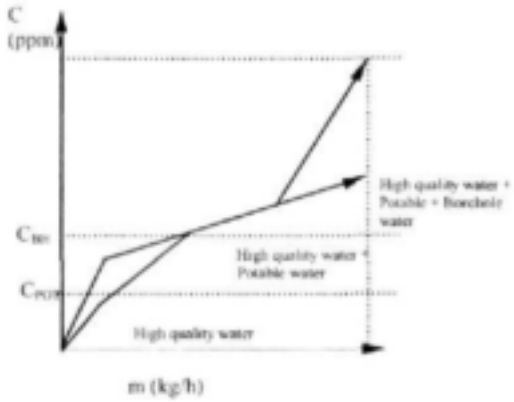


***Figure 2.24** : Targetting using high quality, intermediate quality and low quality water*

On most industrial sites steam is extensively used as a heating medium. On condensation this steam is often a source of a large volume of high purity water. This may appear to present a large opportunity to minimise both the water discharge and intake of the site. However, the temperature of the condensate needs to be taken into consideration in addition to its composition, which leads to the issue of combined water and thermal pinch analysis, for which very little theory or methodology has been developed. In some cases it might be possible to achieve a satisfactory representation of a system by simply treating temperature as a *pseudo-contaminant*, but this device would have only limited applicability.

2.5.2.7 Processes with a Water Loss.

Many processes involve a water loss. Operations such as boiler feed water, cooling tower make-up and reactor feed water are not mass transfer operations but they can, in some circumstances, use spent water from previous mass transfer operations. The involvement of a water loss in these processes means that some, or perhaps all of the water fed to these processes, does not become available for reuse in other processes. Wang and Smith extended their methodology to cover this situation.

Consider how such losses can be included in the analysis. Figure 2.36 shows a limiting composite curve with water supply line matched against it. Now suppose a process with a maximum inlet concentration C_{LOSS} has a specified flow rate loss. This loss is shown in Figure 2.25 as an increase in slope of the water supply line at C_{LOSS}. The flow rate loss dictates the change in slope. The target is now infeasible. Figure 2.26 shows the required increase in flow rate to attain feasibility. The slope of the water supply line below C_{LOSS} gives the freshwater target and the slope above C_{LOSS} gives the wastewater target.

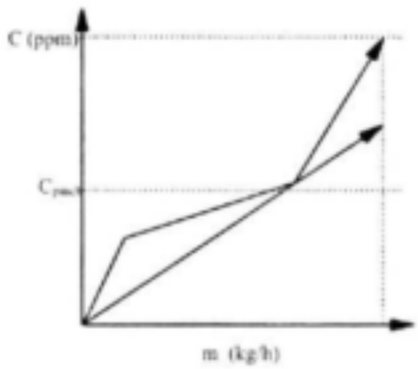


Figure 2.25 : Targetting minimum flow rate with no water loss.

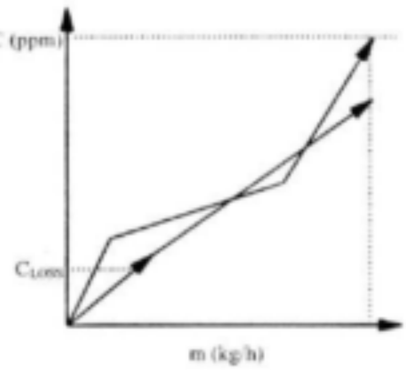


Figure 2.26: Water loss increases the slope of the minimum water supply line and the target is now infeasible

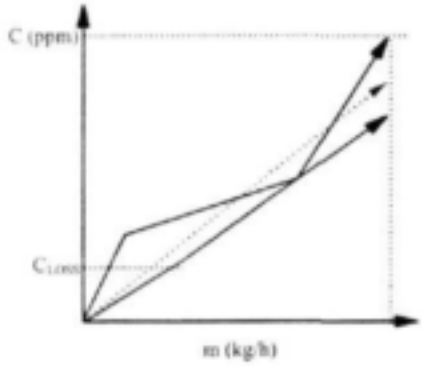


Figure 2.27 : Water flow rate is increased to restore feasibility.

2.5.3 Olesen and Polley (1997)

Olesen and Polley (1997) presented a new procedure for the design of water networks for systems involving single contaminants. It is an extension of Wang and Smith's conceptually based design strategy and uses a *Load Table*, which shows the distribution of duties about the Pinch and the minimum water needs for each operation. The procedure also uses the concept of *Remaining Problem Analysis*.

2.5.3.1 Classification of Operations

The network design procedures reported to date all use some level of numerical analysis. Olesen and Polley (1997) consider these design strategies to be unnecessarily complex. The design of networks for problems having up to four or five individual operations can generally be satisfactorily achieved by inspection. They considered all the possible operations that may be present in a system and classified them into distinct types (Figure 2.28) each of which has distinct design implications.

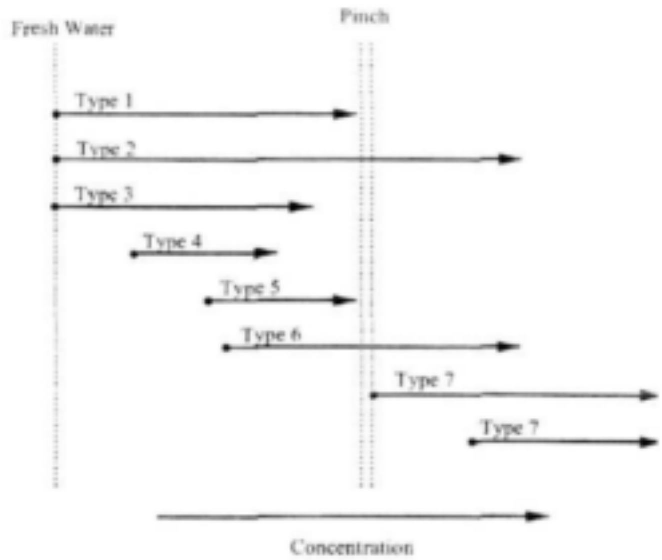


Figure 2.28 : *Stream classification according to Olesen and Polley (1997)*

Type 1. Operations that require fresh water and terminate at the Pinch

These streams can be assigned a fresh water flow rate that provides for a spent water concentration that equals the pinch concentration. This is the minimum flow required for the operation and it does not prejudice the minimum water target. The operation can then be removed from further consideration. This type of operation should be dealt with first in order to reduce the size of the design problem.

Type 2. Operations that require fresh water and terminate above the Pinch.

These streams can be treated in the same manner as ***type 1*** streams. Fresh water is assigned at the minimum flow rate. The minimum flow rate target is not prejudiced. The operation can be removed from further consideration.

Type 3. Operations that require fresh water and terminate below the Pinch.

The spent water from these operations must be reused in another operation prior to the Pinch. Having dealt with operations of ***types 1*** and ***2*** the presence of operations of this type must be flagged before other types of operation are addressed. However, no firm decision on how these operations fit into the network can be taken without reference to the others. The flow of fresh water used for the operation will depend on how the operation is subsequently matched with others.

Type 4. Operations that can use spent water from other operations and terminate below the Pinch.

Again, the spent water from these operations must be reused in another operation prior to the Pinch. If only one operation of this type is present in the system fresh water should be used. The water flow rate will depend on how this operation is subsequently matched with others. If more than one of these operations is present the designer may need to consider using spent water from one operation to feed another.

Type 5. Operations that can use spent water and terminate at the Pinch.

If the system does not contain operations of ***types 3*** and ***4***, fresh water can be used for this type of operation. The treatment is the same as for a ***type 1*** operation; otherwise it may be necessary to use spent water for this type of operation.

Type 6. Operations that can use spent water and terminate above the Pinch.

This is the most difficult type of operation to satisfy. Care and consideration must be taken with regard to both the pinch concentration and the maximum water outlet concentration. The water flow will be limited by the duty on one or other side of the pinch. The designer should start by determining the minimum water flows on either side of the pinch. The minimum water flow required above the pinch is estimated by dividing the above pinch load by the difference between the maximum water outlet concentration and the pinch concentration. The minimum water flow required below the pinch can be determined from the below pinch load and the difference between the water inlet and pinch concentrations. The water used for the operation may be fresh water but it could be spent water from a ***type 3*** or ***4*** operation. The larger of these two water flows is the minimum required for the operation and is subsequently the selected value.

If the above-pinch load is controlling, it is the maximum allowable water outlet concentration that must be met. The required water inlet concentration is then determined from the operation's load and water flow rate. If the below-pinch load is controlling, it is the inlet water concentration that is specified. The subsequent water outlet concentration is computed from the load and water flow.

Type 7. Operations that commence at or above the Pinch.

These operations must use spent water that is at (or above) the pinch concentration. Generally the designer has a significant amount of freedom in the design.

2.5.3.2 Load Table for Network Design

From the discussion of types of operations (particularly that relating to operations of ***type 6***), it is clear that a table listing the above and below pinch contaminant loads and potential flow/concentration profiles would be a useful tool. Such a table is given in Table 2.2 for the single contaminant design problem introduced by Wang and Smith (1994a). The composite curve and minimum water supply line are constructed using the procedure described by Wang and Smith (1994a).

***Table 2.2** : Load table for Wang and Smith's single contaminant problem (After Olesen and Polley (1997).*

			Below the Pinch			Above the Pinch		
Operation	**Type**	**Total Load (kg/h)**	**Load (kg/h)**	**Minimum Flow (t/h)**	**Outlet Concentration (ppm)**	**Load (kg/h)**	**Minimum flow (t/h)**	**Inlet Concentration (kg/h)**
1	1	2	2	20	100			
2	5	5	5	50	100			
3	6	30	2	20	1500	28	40	50
4	7	4				4	5.7	100

This *load table* is constructed by considering the operation classification (***types 1** to **7***), total contaminant load, above and below the pinch loads, above and below the pinch minimum water flow rate for each operation as well as the related inlet and outlet concentrations. (The data defining this problem are given in Table 2.1)

The design for minimum water flow rate is as follows:

Operation 1 is of ***type 1*** and tackled first. The fresh water flow required for the operation is 20 t/h. There are no operations of ***types 3*** or ***4***. Operation 2, which is of ***type 5***, can be treated in the same way as a ***type 1*** operation. Fresh water is used at a flow rate of 50 t/h. Attention is now directed at operations of ***type 6***. Only operation 3 falls into this category. The minimum flow rate required for the above pinch part of the operation will be 40 t/h. Taken over the full operation the maximum outlet concentration of 800 ppm is reached if the water has an inlet concentration of 50 ppm. The minimum water flow rate for the below pinch part of the operation (assuming that fresh water is used) is 20 t/h.

It is seen that the above-pinch part of the operation is limiting. The operation is set as having a flow of 40 t/h at an inlet concentration of 50 ppm. The available freshwater supply is 20 t/h. This can be mixed with spent water from operation 1 (flow 20 t/h, concentration 100 ppm) to provide the exact flow and the required concentration. The only operation remaining is operation 4. This is of ***type 7***. It is easily satisfied using the spent water from operation 2.

The final design (generated by inspection and meeting the minimum water target of 90 t/h) is shown in Figure 2.29. This design is achieved without the complications of the design methods presented by Wang and Smith, namely the use of a grid diagram followed by loop breaking procedures and finally conversion to a conventional flow sheet.

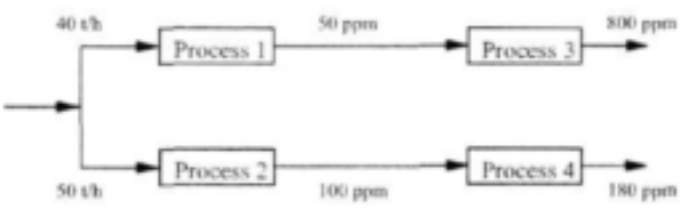


***Figure 2.29** : Final design for Wang and Smith's single contaminant problem.*

The load table concept is a simplification of the Wang and Smith procedure and one would expect it to demonstrate the same limitations as the parent technique. It is however a useful concept and should be kept in mind when tackling a real problem.

2.5.3.3 Remaining Problem Analysis

For larger more complex problems, the designer can be guided using a procedure that could be considered to be analogous to the *Remaining Problem Analysis* used in thermal pinch.

1) An element of the design is developed;
2) the operation is removed from the data set;
3) spent water from the operation is introduced into the data set as a secondary source of fixed flow;
4) Targeting is reapplied to the new data set;
5) The water demand for a system employing the proposed design element now equates with that used in the element plus the target for the remaining operations.

Olesen and Polley (1997) also found that this new design strategy could easily be applied to situations where there are water losses and those where regeneration occurs, without substantially modifying the procedure. This is a useful concept that may be used to substantially reduce both the size and complexity of any given problem.

2.5.3.4 Two Composite Plots

The approach was developed by Buehner and Rossiter (1996), and is represented in Figure 2.30. This procedure uses purity as the vertical axis and water flow rate as the horizontal axis. Each water using process has input and output water streams. There can be several input and output water streams at different purities for a single operation. The input streams of all the water using processes are combined in a demand composite curve in order to define the water demand for the entire plant. The output water streams for all the operations are combined to construct the source composite curve for the entire plant. This is an elaboration of the method suggested by Dhole *et al*. (1996).

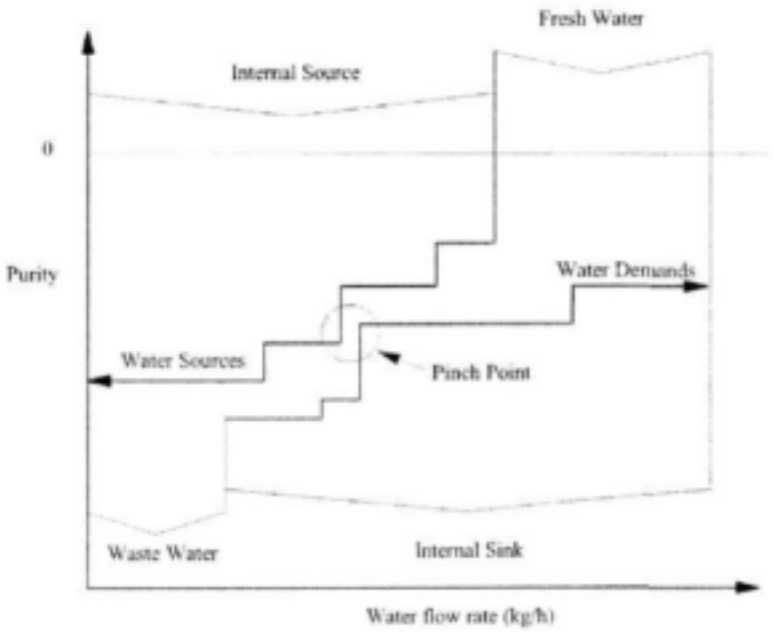


Figure 2.30 : *Demand and source composite overlap indicates the scope for water reuse (Buehner and Rossiter, 1996).*

The overlap between the source and demand composites indicates the scope for reuse. The pinch point limits the available overlap. Minimum fresh water demand and wastewater generations without wastewater mixing are also identified in Figure 2.30.

The water pinch diagram also provides network design guidelines in order to increase water reuse. By combining water sources from units A and B, a mixture of intermediate purity is generated (*Mix*). This mixture now relieves the bottleneck created by the pinch point (Figure 2.31) allowing further overlap and hence greater reuse potential. This is continued until the appropriate network is designed.

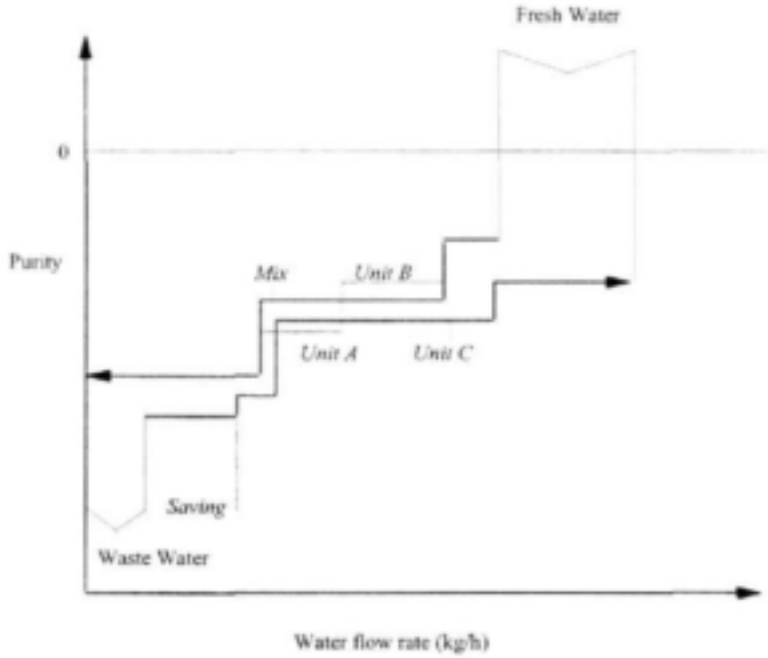


Figure 2.31: *The water pinch diagram guides the designer to identify specific actions to increase water reuse.*

2.6 Mathematical Programming Approach to Water Pinch Analysis

The graphical approaches considered so far provide many valuable insights to the water optimisation problems, but become increasingly difficult to apply when multiple contaminants or special process constraints are involved. They also cannot deal with optimisation in terms of objective functions which include factors other than water use, in particular economic factors. Previous investigators have used mathematical programming for mass-transfer networks, (e.g. Takama *et al.*, 1980 ; Rossiter and Nath, 1995), the formulation which corresponds to the water pinch approach was set out by Doyle and Smith (1997) and extended by Alva-Argaez *et al.* (1998). The WaterPinch software from Linnhoff-March and the programs written as part of this project are largely based on this approach.

2.6.1 Doyle and Smith (1997)

Doyle and Smith considered that a water-using network is not simply a special case of a mass-exchange network, because operations such as cooling towers, steam systems and hosing operations cannot be considered as mass-exchangers. They pointed out that non-linear mathematical programming techniques suffered from difficulties in ensuring that they found the global optimum to a problem, rather than a local optimum, particular for problems involving many variables. Linear programming techniques, on the other hand, can handle very large problems, and global convergence is readily obtained. They therefore presented linear and non-linear formulations of the problem, and proposed a combined linear/non-linear approach to overcome the previously encountered difficulties.

The basic model of a water-using operation (Figure 2.32) is similar to Wang and Smith's fixed-load model (see Figure 2.1), except that:

1) an alternate option is considered, where the mass load is allowed to vary in order to fix the outlet concentration of contaminant ;
2) a water gain or loss is allowed, to model operations such as cooling towers or evaporators.

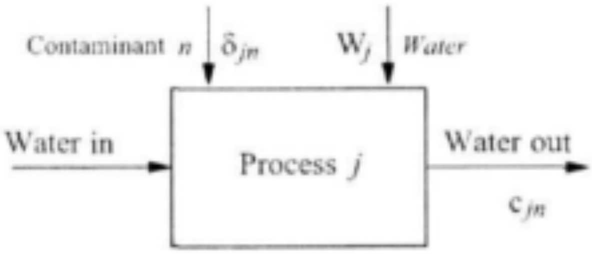


Figure 2.32 : *A water using process.*

The basic concepts of limiting flows and concentrations, and the relationship between them via the mass balances, are exactly the same as in Wang and Smith (1995a) (see **Section 2.5.2.4**).

To automate the procedure for finding the optimal set of connections between units, a *superstructure* for the network is considered (Figure 2.33). This allows, in principle, all possible connections.

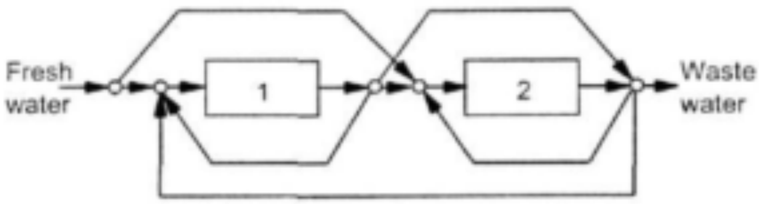


Figure 2.33 : *The superstructure for a simple 2-process network.*

In the original paper, several different versions of the balance equations were given, which made the treatment difficult to follow. Here a somewhat different formulation is used, for compactness and clarity.

The balance over process i can be expressed as

Flow balance: $$\sum_i F_{ij} + \sum_w F_{jw} - \left(\sum_i F_{ji} + \sum_k F_{jk} + W_j\right) = 0 \qquad (2.7)$$

Balance for component n: $$\sum_i F_{ji}\, c_{in} + \sum_k F_{jk}\, c_{kn} + \delta_{jn} = \left(\sum_i F_{ji} + \sum_k F_{jk} + W_j\right) c_{jn} \qquad (2.8)$$

Where

F_{ji} is the flow of (reused) water from outlet of process i to inlet of process j
F_{jw} is the flow of (used) water from outlet of process i to waste sink w
F_{jk} is the flow of (fresh) water from source k to inlet of process j

C_{in} is the concentration of ion n in outlet stream from process i
δ_{in} is the mass gain of contaminant n over process i
W_i is the water gain over process i.

Balances of this form exist for each of the P processes and k contaminants in the system, and can be viewed as the basic set of process constraints. Specific limits on flows and concentrations, for a particular system, will form additional constraints.

To complete the formulation, an objective function must be defined to provide the basis for optimisation. A rather general form for the objective function was proposed, representing fixed and variable costs associated with each stream in the system, to be minimised:

$$\Omega = \sum_{i,j} \left[a_{ij} + b_{ij}(F_{ij})^{c}\right] \tag{2.9}$$

(In fact, this form fails to address an important practical issue, namely where the cost associated with a particular stream is dependent on the contaminant load, rather than just the flow rate, however there is no particular problem in including terms to represent this.)

This formulation of the problem has non-linearities in the objective function (Eq. 2.9) and in the component balances (Eq. 2.8). It should usually be possible to use a linearised objective function as an approximation, but, in the case of fixed contaminant loads, the component balances are intrinsically non-linear because the terms which are products of flow rate and concentration, since both are variables in the problem. In the case of fixed outlet concentrations, however, Eq. 2.8 is linear in the flow rates, since the concentrations are then known constants. Thus, if all processes in the system are of the fixed-outlet-concentration type, the problem could be formulated to a linear programming (LP) optimisation. Although this is a most unlikely scenario, it is reasonable to suppose that, in an optimised system, the concentrations will approach their limiting values. This means that the LP solution could be taken as a good starting estimate for a non-linear programming (NLP) optimisation. Providing a good starting estimate is the most important means of achieving satisfactory convergence in non-linear programming. This rationale forms the basis of the linear/non-linear approach.

2.6.2 Alva-Argaez, Kokkosis and Smith (1998)

The extension to the Doyle and Smith treatment consisted of noting that, once a set of flow rates had been obtained from the linear-programming solution, which assumes that the outlet concentrations are at their limiting values, one can calculate the corresponding set of concentrations, and determine where the assumptions are in error. If the calculated concentrations are below the limits, the errors are of no consequence. For concentrations which exceed the limits, the errors can be added into the objective function to be minimised, so that running the LP algorithm again will tend to drive the errors to zero. This provides the basis for a method which uses a series of LP optimisations which converge to the NLP solution, taking advantage of the particular mathematical structure of water pinch problems.

A further refinement introduced binary variables corresponding to each possible connection in the network. For these, a value of 1 indicates that the connection exists, and a value of 0 that it does not. This formulation allows automatic control of features such as the elimination of streams which fall below a specified flow rate, or the maximum number of connections allowed in the network, to avoid excessive complexity. These variables move the optimisations into the class of *Mixed Integer* (MI) programming - once again mixed integer linear programming (MILP) is very much more tractable than mixed integer non-linear programming (MINLP).

2.7 Pinch Analysis of Batch Processes

All the methodologies discussed above deal with continuous processes. It was initially thought that the application of pinch analysis techniques in batch processes would have very limited benefits due to the intrinsic time constraints. Moreover, the incorporation of process integration in batch processes was perceived to lead to reduced flexibility, which is the main advantage of batch processes. There was also a general understanding that batch processes have intrinsic variations which eventually lead to deviations from predetermined schedules. This would make targeting extremely difficult, if not impossible. Moreover, pinch analysis was regarded as only an energy optimisation technique which would not have much significance in batch operations, since energy usually constitutes a small component of batch operating costs (Obeng and Ashton, 1988).

2.7.1 Batch Heat Transfer Pinch Analysis

The use of pinch analysis in the optimisation of batch heat-transfer operations only started following publications by Kemp and MacDonald (1987), Obeng and Ashton (1988) and Kemp and Deakin (1988).

Obeng and Ashton (1988) drew the comparison between the Time-Temperature Cascade (Kemp and MacDonald, 1987,1988) and the Overall Plant Bottleneck (OPB) approaches. The cascade approach generated a time dependent analysis of energy flows with respect to time and temperature. This was achieved by setting up the problem table analogous to that in the analysis of continuous processes (Linnhoff and Hindmarsh, 1983), but allowing heat to be cascaded with respect to time and temperature. Other than setting the energy targets, this approach also allowed the heat storage opportunities to be identified. In setting energy targets, the OPB approach first removed the time constraint by using the concept of the *Time Average Model* (TAM). In this model the heat loads were averaged over a chosen period followed by the construction of the hot and cold stream composite curves as in continuous processes (Linnhoff and Hindmarsh, 1983). The *Time Slice Model* (TSM) was then used to set targets based on a chosen schedule. The time slices were constructed by plotting each of the process duration times on a time plane. The target was then set by calculating the energy demand in each of the time intervals. This target was then optimised by increasing the direct heat transfer opportunities between hot and cold streams by schedule modification. The schedule modification was achieved by allowing some processes to start earlier, end later or finish earlier than prescribed in the initial schedule. Attention was drawn to the fact that these process changes could have an impact on plant capacity, flexibility, process yields as well as energy consumption.

It was then concluded that the TAM target could be achieved by modifying the initial schedule using the time slice diagram. The cascade approach also yielded the same energy target as the TAM when applied to repeated batch operations. The cascade analysis was, therefore, found to be rigorous with respect to the energy target, but not with respect to the heat storage capacity, since this is highly dependent on the initial assumptions made. The implication was that the TAM could be used as a shortcut in setting the targets. This was, however, later reproved by Kemp and Deakin (1989). Both the cascade analysis and OPB techniques did not include cost factors.

Kemp and Deakin (1989) produced a series of three papers on cascade analysis. In their first paper, the application of cascade analysis in setting energy targets was revisited. This was compared to the OPB approach presented by Obeng and Ashton (1988). Rather than confining the targeting procedure to simple scheduling diagrams, the thermodynamic potential of hot and cold streams to exchange heat was explored in sufficient detail. The shortcomings of using the TAM in dealing with batch processes was highlighted by using a simple batch process flow sheet with one inlet and one outlet stream. Each of the streams was fully specified in terms of thermodynamic properties. The conclusion was that an analysis method that does not allow for variations with time, like the TAM, is inadequate for even the simplest batch processes (Kemp and Deakin, 1989). This paper also introduced the use of a three dimensional cascade plot to aid visualisation of heat flows and the mathematical formulation of the technique for computer programming.

In the second paper of the series, the application of cascade analysis in the design of *maximum heat exchange* (MHX) networks was presented. Attention was drawn to the fact that, unlike continuous processes, batch processes do allow the transfer of heat across the overall pinch without compromising the maximum efficiency of the network. The implication is that the pinch violation rules which apply to continuous processes (Linnhoff and Hindmarsh, 1983; El-Halwagi, 1997) do not apply to batch processes. Rescheduling opportunities were also divided into four broad classes and their effect in the overall targeting procedure assessed.

The third paper of the series presented a case study on the application of pinch analysis in a system of batch operations from speciality chemicals plant. The problem formulation had eight cold streams and five hot streams with their supply and target temperatures, start and finish times and heat capacity flow rates specified. The study showed that the application of cascade analysis to this problem could lead to 28 % and 12.2 % savings in energy consumption using heat storage and direct heat exchange, respectively.

In 1995, Wang and Smith introduced an entirely new methodology for the setting of energy and water demand targets in batch operations. The methodology was initially applied to the integration of heat transfer operations including the utility system design, and later applied to wastewater minimisation. In their approach (Wang and Smith, 1995b), time was taken as the primary constraint and temperature (for heat transfer operations) or concentration (for mass transfer operations) taken as secondary constraints. This constituted a slight variation from the methodologies published by Kemp and Deakin (1989) and Obeng and Ashton (1988), in the sense that these authors did not prioritise with respect to temperature and time constraints. However, it is worthy of mention that the nature of the cascade analysis is such that temperature is given first preference to time, but this does not necessarily mean that temperature is treated as the primary constraint. The implication of the time constraint in batch operations is shown in Figure 2.34. If the schedule is such that the energy source (in the case of heat exchangers) or the water source (in the case of water networks) appears before the sink, then it is possible to transfer energy or reuse water from the source to the sink. Nevertheless, if the source appears after the sink in the time schedule, time constraints will forbid the transfer of energy or reuse of water.

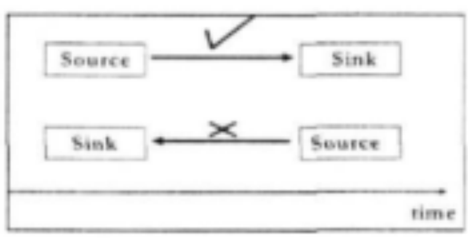


***Figure 2.34** : The implication of the time constraint in batch operations.*

As with continuous processes, batch operations are also constrained with respect to driving forces, i.e. temperature and concentration for heat and mass exchangers, respectively. The implications of temperature and concentration constraints are shown in Figures 2.35 (a) and (b), respectively. If the hot stream is supplied at a lower temperature than the cold stream, then the temperature constraints will forbid the transfer of heat from the hot stream to the cold stream, Fig. 2.35 (a). Similarly, if the rich stream is supplied at a lower concentration than the lean stream, concentration constraints will forbid the transfer of mass from the rich stream to the lean stream, Fig. 2.35 (b).

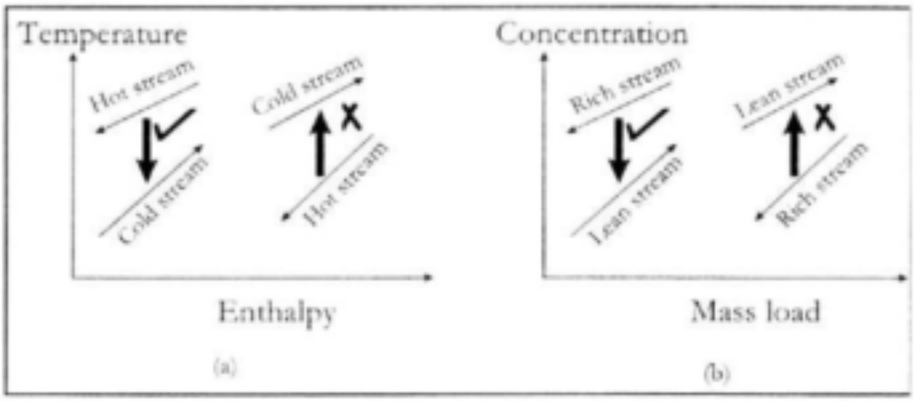


Figure 2.35 : *Effect of (a) temperature and (b) concentration constraints in batch operations.*

The foregoing discussion puts more emphasis on the time constraints, however, for heat transfer to be feasible, temperature constraints must also be satisfied. To introduce temperature constraints in the targeting procedure, Wang and Smith (1995) adopted the Problem Table Algorithm of Linnhoff and Flower (1978). In this algorithm the designer initially sets the minimum temperature difference (ΔT_{min}) between the cold and the hot streams. In order to ensure that this temperature difference holds throughout the temperature intervals, the hot stream temperatures are reduced by $\Delta T_{min}/2$ and the cold stream temperatures are increased by $\Delta T_{min}/2$. Applying the time constraint analysis in each of the temperature intervals ensures that both time and temperature constraints are satisfied.

Having demonstrated the application of their methodology in setting energy targets and identification of storage requirements, Wang and Smith, (1995b), extended the application of this methodology to utility system design. This was based on the realisation that, in general, the capacity of utility systems for batch operations is based on peak demands. This implies that for the off-peak times the utility systems operate inefficiently due to the loss of surplus energy as shown in Figure 2.36.

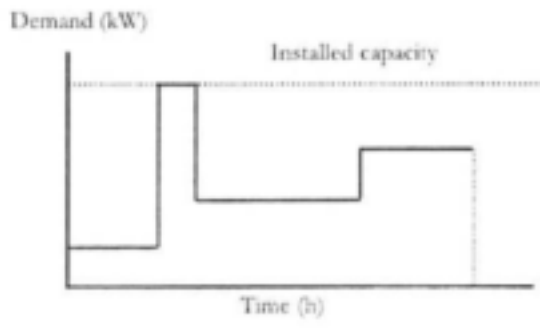


Figure 2.36 : *Heating demand of batch processes over time.*

The methodology was applied to the sizing of accumulators to cater for increases in energy demand. It was also used as a formal tool in making a choice between increasing the capacity of the existing plants and providing an adequately sized accumulator to handle variations in energy demand. An example was given where a choice had to be made between replacing one of the boilers which had come to the end of its life in a plant consisting of two boilers, and providing an accumulator which was going to operate with the remaining boiler. The Wang and Smith analysis showed that the installation of an accumulator and the removal of the old boiler was a viable option.

2.7.2 Batch Water Pinch Analysis

Wang and Smith (1995b) introduced their method for analysing the water requirements of a set of batch processes by way of a single illustrative example, which set out the framework and context within which the method may be applied. The specification of this hypothetical problem contained a number of implied assumptions, which were not explicitly discussed, and which constitute important limitations on the type of processes which can be considered.

The problem was specified in terms of a set of water streams, each characterised by a flow rate, a start time, an end time, and maximum limits for the inlet and outlet concentrations of a single contaminant. At first sight this appears to be a rather general framework for representing such problems, apart from the obvious restriction of considering only one contaminant. However, the way that these specifications were used in their method implied some less immediately obvious assumptions:

1) The processes involved are not truly batch processes (at least, with respect to the water streams), but operate in a continuous flow mode between their starting and ending times.
2) The primary purpose of each water stream is to absorb a fixed mass-flow of contaminant from the process.
3) The water flow-rates are fixed.
4) Of each pair of inlet and outlet concentration limits, one is fixed directly in terms of concentration, and the other is determined from it, together with the water and contaminant flow rates, by material balance.

Targeting was performed by cascading water from one concentration interval to the next, until the last concentration interval. Within each concentration interval, water was cascaded from one time subinterval to the next without degradation. This appears to be the mass transfer version of the targeting procedure presented for heat exchangers. Methods for allocating water so as to meet the targets, and for establishing intermediate storage requirements were presented.

When an attempt was made to apply these techniques in practice it became apparent that these assumptions do not always apply, and that modifications would be needed to account for the different circumstances that can arise. Some possible variations are:

1) The semi-continuous mode of operation envisaged by Wang and Smith does not seem likely to be encountered commonly in practice. Frequently processes operate in *completely batch* mode, by which is meant that a fixed quantity of water is added to the vessel at the start of the period, and remains there until it is discharged at the end of the period. This has quite different implications for reuse potential from the *semi-continuous* case. Firstly quantities rather than flows are relevant, and secondly the effect of time on the problem is almost completely reversed. In the semi-continuous case, effluent flows continuously, and so is available for reuse during the time when the process is active. To reuse it at any other time is problematic, in that it requires provision of a storage facility. In the completely batch case, the water is needed in the process during the time when it is active, and is not available for reuse until the process comes to an end. The issue of storage also presents itself differently, as the reactor

vessels provide inherent storage facilities which can potentially be used when they are not active in the process.

2) Assumptions ii) , iii) and iv) above between them contrive to fix the water quantity, contaminant load and inlet and outlet concentrations as equality constraints. However, a number of variations are possible in the way that the process constraints on quantity (or flow) and concentration present themselves. For instance, it could happen that there is no direct specification of the water quantity in a particular stream, as long as the contaminant load and outlet concentration constraints are observed. The reactor vessel will probably have maximum and minimum levels for effective operation. In such a case the water quantity and inlet concentration fall away as equality constraints, to become inequality constraints, thereby changing the nature of the optimisation problem.

2.8 Conclusions

The concepts of pinch analysis, originally developed for the optimisation of complex heat exchange systems, has undergone extensive elaboration and adaptation to various fields, water and effluent management being of particular interest here. This process of elaboration and adaptation continues to gather momentum, and it seems probable that it will eventually lead to a generalised *resource pinch analysis*, which includes the current branches of the theory as special cases. Essentially, pinch analysis involves optimising the use of the resource, subject to the constraints which apply to the particular system involved. The generalised theory provides insights and analogies which translate between different branches of application, the adaptation and specialisation arises mainly from the specific practical considerations which apply to the use of a particular resource.

Water pinch analysis faces some special challenges because of the almost universal use of water in industrial systems for a great variety of purposes. The straightforward analogies with energy transfer are limited, because water quality can seldom be expressed in terms of a single measure, in the way that temperature represents the quality of energy. Hence, single contaminant theory has little applicability, and has at least to be extended to deal with multiple contaminants. Many recent advances have been concerned with addressing this aspect.

In practice, however, multi-contaminant theory still has fundamental limitations, as it treats water as the single resource in the analysis. Often water serves as the carrier for other resources, for instances chemical reagents, chemical products and energy, which may have complex interactions with each other, both in the physical and economic senses. This area has received very little attention in the literature up to now, although some work is starting on combined heat and water pinch analysis. (Savalescu and Smith, 1998).

Practical case studies involving water pinch analysis are also very sparse in the current literature. As these appear, it can be expected that they will stimulate the development of new theory to deal with the new issues that they raise.

3 A GUIDE FOR WATER PINCH INVESTIGATIONS

In this project, a number water pinch investigations were undertaken at industrial sites in order to promote the concept to South African industries and to build local capacity to use it effectively. Each of this case studies had its own successes and failures: in this chapter an attempt is made to distil the lessons learned into a guide which will assist someone who wishes to conduct such an investigation.

The overall course of a water pinch investigation may be outlined as follows:

- selection of the system boundaries;
- identification of the scope of the investigation;
- selection of contaminants;
- connectivity and network reduction;
- data gathering ;
- data reconciliation;
- pinch problem formulation;
- optimisation;
- implementation.

It is seldom possible to proceed in a neat linear fashion through these steps, as later steps may expose issues which require earlier ones to be revisited.

Furthermore, despite water pinch analysis being a rigorous and technical approach towards the rationalisation of freshwater use and effluent production within a factory, the success or failure of the investigation relies heavily on the interactions between people in the investigation.

3.1 Involvement of Factory Personnel

One of the barriers that have hindered the rapid adoption of water pinch analysis techniques has been the gap that remains between the pinch 'expert' and the personnel who run the factory. The approach and skills involved in mathematical modelling and optimisation are often at odds with those involved in the practical running of a plant, however the task of the modeller is to capture the critical operational constraints and objectives of the process in a mathematical representation. It follows that there must be a very close co-operation between the modeller and the practitioners, and they need to have a good understanding of each other's requirements and concerns. In this project, the difficulty was accentuated by the academic/industrial division between the parties, with the differences in objectives that that entailed. In particular, problems with the interactions between the researchers and the factory management played a significant role in the failure of the SA Tioxide investigation (**Section 7.1**) to achieve useful practical results.

3.1.1 Management Commitment

The main aim of a pinch analysis is to identify changes to the configuration of a plant which will lead to more efficient use of water. This obviously can have a major impact on the running of the plant. Unless there is a willingness on the part of management to consider implementing such changes, undertaking a water pinch analysis has little chance of a completely successful outcome. This has been a particular problem with doing pinch analysis on an academic research basis. The willingness to allow a factory to be used as the subject of an academic research analysis is very different to the willingness to implement design changes based on its outcome. Another barrier that can exist is that, where there have been water conservation programmes in place, the management may not be convinced that it is possible to achieve significant further improvements, and so may not be willing to wholeheartedly commit resources to the investigation.

3.1.2 Technical Personnel

It is vital that the factory should designate a technical liaison person to interact with the water pinch investigator, and that this function should be assigned as part of his or her official duties, with an adequate time allocation. The person should be experienced in the plant's technical issues and operating constraints, and able to relate these, in a broad conceptual way, to the mathematical models. A person of this calibre is usually already very valuable to the factory, which is one of the reasons that management commitment is so necessary.

Of the investigations that proved successful, the liaison person was the station chemist at the Lethabo Power Station (Carl Woodhouse), a senior engineer at Polifin (Ron Sayer) and a process engineer at Sanachem (Thokozani Majozi).

3.1.3 Communication

From the above discussion it is clear that there must be very good communication between the water pinch analyst and the factory personnel in setting up the pinch models and obtaining data. However, during the investigation at AECI Bioproducts, another less obvious lesson was learned. *After the data has been obtained, it is important that communication be maintained during the initial modelling and optimisation phases, because the investigation does not proceed linearly from data gathering through modelling and optimisation to implementation.* What happened during the project was that several months were taken up with modelling and optimisation, until results were obtained which were deemed good enough to present to the factory. At the presentation of these results, several issues were raised which had been previously overlooked, and some of the difficulties which had caused the long delay were due to aspects of the model which did not represent the factory correctly, and so were not actually relevant. The conclusion was that *it would have been much more efficient to have presented preliminary and incomplete results much earlier, so as to engage the factory personnel in the process.* Since it is practically inevitable that the investigation will go through a number of iterations, these should begin as early as possible.

3.2 Selection of System Boundaries

Water pinch analysis seeks to optimise the water use within a specified system through integration of the of the requirements of the various parts of the system. Clearly the results that can be achieved are completely dependent on what constitutes the system to be considered. In general, the larger the system, i.e. the more individual operations it contains, the greater the potential benefits of integration, however the more difficult it becomes to operate on an integrated basis. The difficulties may be geographical (units too far apart), temporal (units subject to different scheduling constraints) or organisational (units operated by different divisions or organisations with different objectives and priorities). The selection of what should be included in or excluded from the analysis is an important preliminary step for a pinch analysis.

If the system is too small, the pinch analysis will yield little or no benefit. The *size* of the system, in this context, is not necessarily related to the volumes of water involved, or even to the complexity of the flows. It is usually related to the *number of process subsystems which were not previously operated together on an integrated basis.* In the South African context, the relative scarcity of water has meant that companies have for many years been under pressure to reduce water consumption, and one can expect that many individual operations already use water efficiently. This means that one needs to look for opportunities where several such subsystems can be integrated.

Thus, at the Lethabo power station (see **Chapter 6**), it was found that the power station water circuits were already operating close to optimally, if the system boundary was drawn around the power station. However, if the associated coal mine was considered to be part of the system, the pinch analysis suggested significant changes to the operating strategy. At the Mondi Merebank paper mill (**Chapter 7**), the pulp preparation plant and the individual paper machines were effectively countercurrent operations, with very little scope for improvement when considered separately.

It is self-evident that the difficulties of operating and controlling a system will grow as the number of subsystems increases, or the diversity in their operating objectives increases, however none of the investigations undertaken during this project reached a point of providing an opportunity for practical experience of this issue.

3.3 Scope of Investigation

Pinch analysis, in the broadest sense, is concerned with the optimal use of resources (such as energy or materials) in a multi-process system. Water pinch analysis, a special case of mass-exchange pinch analysis focusing on the optimal use of water, has developed due to the widespread use of water as a multipurpose resource. Because of the wide range of processes which use water, a particular approach has been developed in the literature which involves a specific set of approximations and assumptions. These are chiefly that the system can be divided into *process streams* and *water streams*. In this conceptual framework, the process streams are fixed by the technology of the process, and come into the analysis only as boundary conditions: that is, their flow rates and compositions are considered invariant. The mass transfer between the process streams and water streams is represented implicitly by contaminant mass loads transferred to the water, with concentration limits being applied to the water streams. This model applies very well to an oil refinery, for example.

The standard approach of pinch analysis is to consider the core technology of the process as fixed while optimising the resource allocation network. In the larger problem of optimising the entire process, changing the technology would be considered in a separate step, after which the pinch analysis would have to be repeated. The term *utility-water pinch analysis* is proposed to describe the methodology which is currently standard.

This standard approach will often have limitations for systems where the process streams, i.e. the streams which embody the technology of the process, are themselves water streams. A paper mill and a hydrometallurgical process are examples of this type. The term *process-water pinch analysis* is proposed to describe the case where process streams are included, with the understanding that utility water streams would also be included in such an analysis. Following this terminology, most of what appears in the literature is utility-water pinch analysis, and a comprehensive theory has yet to be developed for process water pinch.

The distinction between process and utility pinch analysis was not clearly understood during the early investigations of the project. At SA Tioxide, where a large part of the process is hydrometallurgical, we attempted to apply utility-pinch methods where a process-pinch analysis was required, which yielded no usable conclusions. At Polifin, the first study by Gardner focussed on the internal use of NaOH and HCl in the factory, and concluded that 'conventional pinch theory' was inadequate to deal with the issue. Gardner developed a new methodology, which was rather specific to the situation at Polifin. In hindsight this can be seen as a case of discarding utility pinch analysis and venturing into process pinch analysis.

Since a comprehensive theory for process-pinch analysis has yet to be developed, in most practical cases one has to attempt to fit the problem into a utility pinch analysis framework, by classifying water streams as either process streams or water streams. *Process streams are then excluded from the analysis*, except possibly as fixed sources or sinks of water, with fixed compositions.

3.4 Selection of Contaminants

Within the context of a water pinch investigation, the waterborne species which restrict the reuse of water in the system are termed *contaminants*. The identification of these species is done simply by questioning what prevents the reuse of a water stream in a particular area of the system. Contaminants may be single entities such as ions or molecules (e.g. Ca^{2+} ions) or aggregated groups e.g. total dissolved solids (TDS).

In some cases it becomes necessary to distinguish between contaminants and *reagents* which are introduced deliberately (this can be seen as another aspect of the process/utility question). Some like NaOH may be a reagent in one part of a process, and a contaminant in another. One may have to consider the part of the system where a solute is a reagent as an invariant part of the process, i.e. excluded from the pinch analysis.

Because the pinch analysis will consider re-routing streams to services which are different to those currently in place, it is important that the limits are found for all relevant contaminants. Thus there should be global set of contaminants which is applied to all streams and nodes. If this is not feasible for certain streams or nodes, then these may have to be excluded from the system analysis. Identifying all the relevant contaminants at the outset of the investigation may be very difficult, because a configuration suggested by the pinch analysis may bring a contaminant into prominence which previously was not critical. This provides another reason why the water pinch analysis often requires an iterative approach.

Contaminants which can only appear in one or two streams can usually be left out of the analysis and handled by common sense. For example, in the case of the Lethabo power station, suspended solids and carbonates go directly to sludge in the softening clarifiers (assuming that these are operating correctly), and have no effect on any other streams. These components were therefore left out of the model.

Not all water quality determinants are suitable to be taken as contaminants. pH is a case in point, as it not a conserved quantity in the material balance sense. The process unit models currently used in water pinch analysis are based on simple material balances, and cannot predict the pH resulting from combining streams.

Furthermore when selecting multiple contaminants, it is important that each individual contaminant is independent of the others. For example, an ion such as Na^+ should normally not be used with total dissolved solids (TDS), since Na^+ forms part of the TDS measurement.

3.5 Data Gathering

The basic information required for a water pinch analysis consists of a set of the following items for each water using unit operation in the system under consideration:

- volumetric requirement of water at the inlet(s) of the unit ;
- volume discharged from the outlet(s) ;
- water lost or gained in the unit (e.g. by evaporation) ;
- mass loads of contaminants transferred to or from the water by the unit ;
- limiting concentration for contaminants in the unit.

In its simplest formulation, water pinch analysis considers the design of a new water using system, in which case this kind of information should be provided as part of the design specifications. However it is much more common for a water pinch analysis investigation to be applied to an existing water using system. In such a case, flow and concentration data for the various operations will be available as measurements from the existing system rather than design specifications. These will have the advantage of being proven in practice, but the disadvantage that, as they almost certainly come from a non-optimal system, they do not represent genuine limits for the processes. If they are treated as such, it may well happen that the pinch analysis will not be able to come up with significant water savings.

A data gathering and mass-balancing exercise is therefore a major part of a water pinch investigation: indeed, the experience of this project has been that it has been the most difficult and time-consuming aspect. Its objective is to obtain a flow and contaminant balance for the existing water system. This will be set up in the context of a set of nodes to be connected by water streams. Each node will correspond to a process which may have quantity and quality requirements, and mass loads of contaminants which are either added to the water stream or subtracted from it. *The purpose of the flow and contaminant balance is to estimate these requirements and limits from the existing operating data.*

3.5.1 Connectivity

It is often convenient to start the data gathering from a flow sheet, which shows how units are connected by flows in the existing plant. It is not essential to approach it this way, because the pinch analysis will be concerned with finding the optimal connectivity, which may be quite different from what exists. However a flowsheet is a standard way of representing such systems, which engineers are familiar with.

For water balance purposes, the flow sheet should generally represent all water-containing streams on the plant, whether these will be included in the pinch analysis or not. The exception to this guideline will occur when a stream is completely isolated from the streams that will be included in the analysis, such that no water can be transferred to or from them by the excluded stream.

In drawing up a complex flowchart, it can easily happen that various topological problems arise as a result of connection errors. These can often be difficult to find, and lead to situations where the associated mass balance equations have no solution. This problem is inherent to the flowchart-based approach. Because the Linnhoff-March WaterTarget™ software, which is used to assist the data gathering process, takes a flow sheet as its starting point, it has sophisticated algorithms to check a flow sheet for topological consistency.

During the investigation of the Lethabo Power Station (**chapter 6**), the approach that was taken did not use a flowchart as a basis for the data gathering exercise. This happened because the main source of data was a set of monthly water usage reports which were routinely prepared by the station, and which already contained figures that were largely balanced and reconciled. Figure 3.1 is a flow sheet that was prepared up to aid visualisation of the system when drawing up the model.

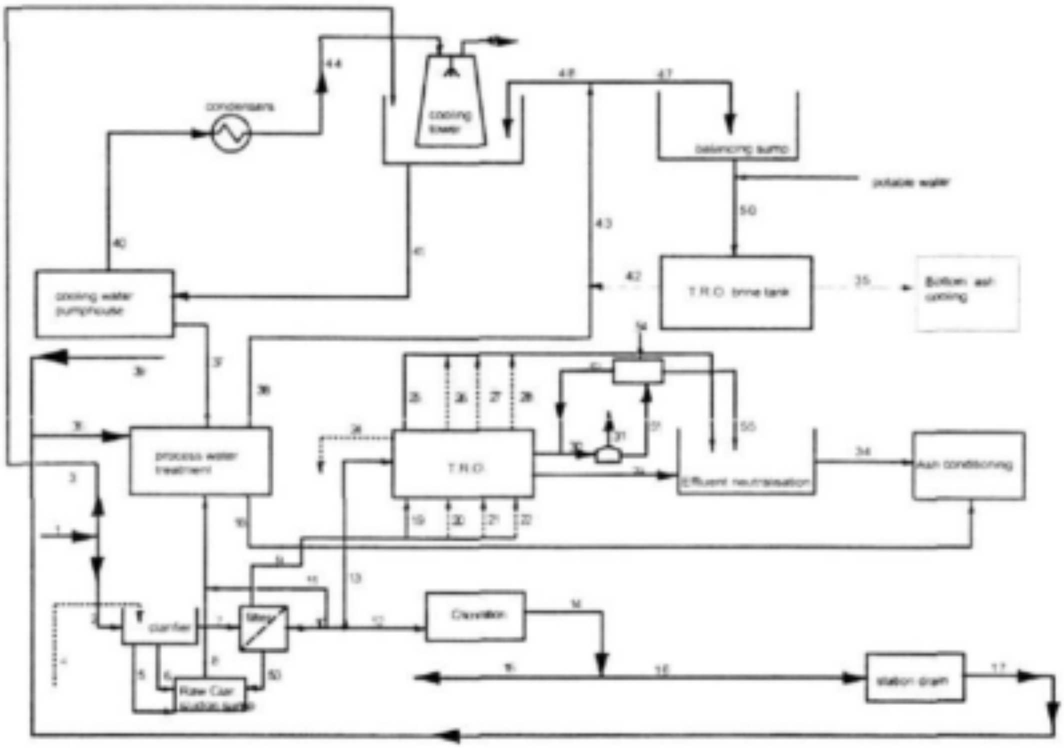


Figure 3.1: *A moderately detailed flow diagram of the Lethabo Power Station Water Circuits. Numbers indicate individual plant streams.*

This diagram was only used indirectly to prepare the next diagram, Figure 3.2. This shows the pinch model component blocks which were extracted from the flow sheet. Its notable feature is that it shows no connectivity between the components whatsoever, since pinch optimisation will be used to determine how the components should be connected.

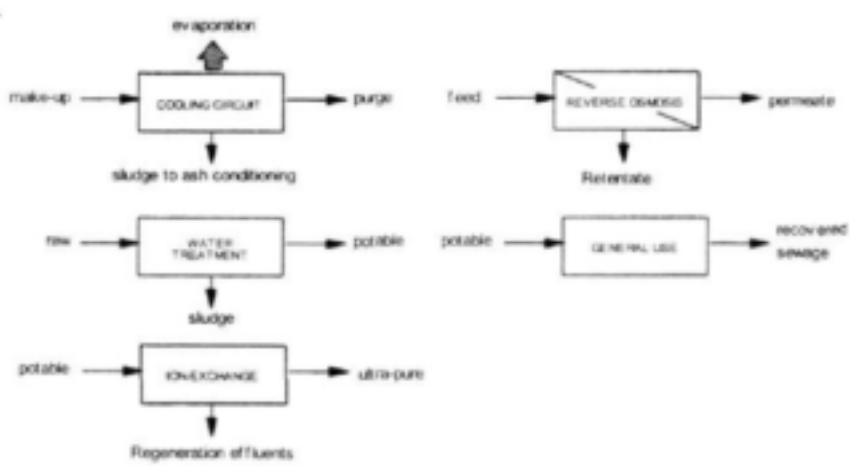


Figure 3.2: *Pinch model components for the Lethabo Power Station.*

During the investigation of the Polifin chlor-alkali plant, which had somewhat more complex water circuits, an attempt was made to make this process of *network reduction* more formal and systematic (see **Section 3.5.2**).

3.5.2 Network reduction

Network reduction forms an important conceptual step in the water pinch investigation. This step sees the transformation of the existing process network, containing nonessential process features, into a more specific network which contains only those aspects of the existing process which are essential to the optimisation problem - this network is then optimised in the solution stage of the investigation. Network reduction is a non-quantitative exercise requiring only a knowledge of the process structure and general operation of units within the process. The results from this exercise may be used as a tool to guide the data collection process.

In terms of standard water pinch theory, network reduction relies on the distinction being made between what is considered a process stream and what is considered a water stream. It is important to be aware that a standard water pinch analysis does not change the *process* in terms of the progression of raw materials to products - it is therefore possible to group operations involving process streams together. Water pinch further does not alter the functioning of unit operations; hence, provided the quality of water permitted into the operation is acceptable to that operation from the beginning, it is possible to disregard what takes place beyond the point at which water enters the operation.

Consequently, individual unit operations may be grouped or split, as necessary, into *functional operations*, *functional demands* and *functional supplies*. A functional operation is *any grouping of operations over which a contaminant concentration difference exists*. This categorisation includes fixed mass-load operations as well as other operations such as backwash stages on filters. A functional supply refers to a *group of operations which produce a supply of water of a particular quality, available to the rest of the system*. A functional demand is similarly a *group of operations requiring a supply of water of a particular quality from the system*. These 'groups' of operations may consist of multiple operations, single operations or even individual stages of operations.

Presented below is a series of heuristics to guide network reduction. A simple example will be used to illustrate the procedure at each point. Figure 3.3 represents the process flow diagram for a section of a hypothetical process in which a raw material is converted into a crystalline product. Water is used within the process in various capacities - dilution, mass-load removal, heating and cooling, and different effluents are produced. Some degree of water reuse does already take place in the network through the reuse of wash water and condensate.

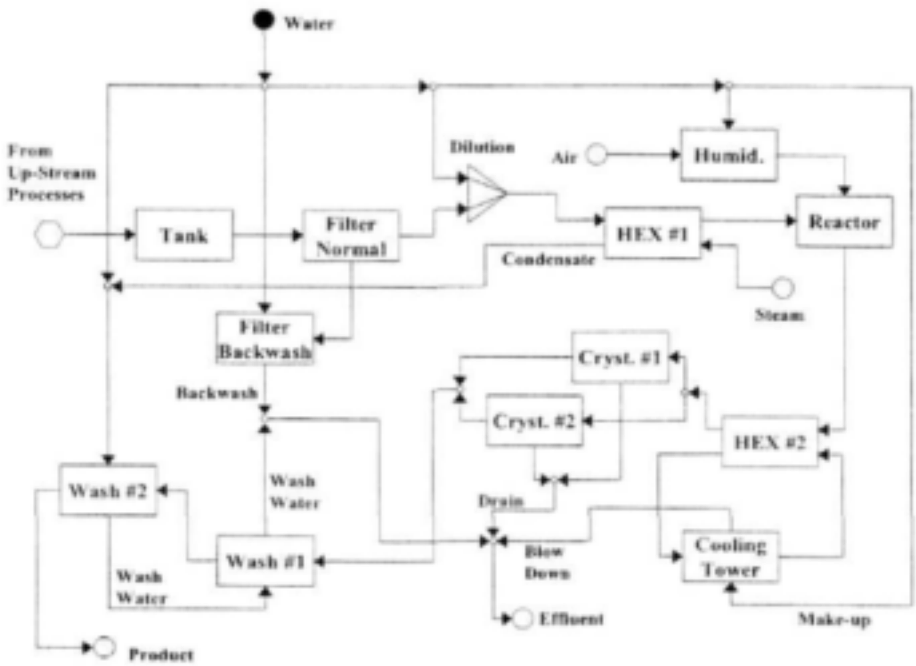


Figure 3.3: *Flow diagram of a hypothetical process.*

Procedure

i) Represent all phases of the process operation appropriately and as they occur on the plant. For example, consider the clarifying filter presented in Figure 3.3. The normal operation of the filter is represented as an inlet stream producing a cleaner outlet stream. The material removed by the filter is represented as a stream from the normal operation stage to the backwash stage - this material is removed by a backwash stream.

ii) Eliminate all irrelevant streams from the network. These are the streams that do not involve water and are not involved in contaminant mass loading or removal. In the hypothetical process, Figure 3.4, the air stream is eliminated from the network.

iii) Split all indirect contact operations present in the network according to the number of independent paths used by the materials flowing through the operation. The heat exchangers HEX#1 and HEX#2 represented in Figure 3.4 are each split into two operations (HEX#1a, HEX#1b, HEX#2a, HEX#2b) representing the passage of material through the shell sides and tube sides of these exchangers.

iv) Eliminate all storage vessels from the network by grouping them with adjacent units. The tank in Figure 3.4 is grouped with the adjacent filtration operation.

v) Eliminate all single phase split operations (resulting from step iii)) from the network by grouping them with adjacent operations. In Figure 3.4, HEX#1a and HEX#2a are grouped with the adjacent reactor and HEX#2b is grouped with the cooling tower.

vi) Represent all parallel equipment present in network by a single unit of the same type, but of combined capacity. This grouping applies only to parallel equipment of the same performance and type, e.g. filters. In Figure 3.4, Cryst#1 and Cryst#2 are grouped together. Figure 3.4 represents the nodal diagram for the process for step vi).

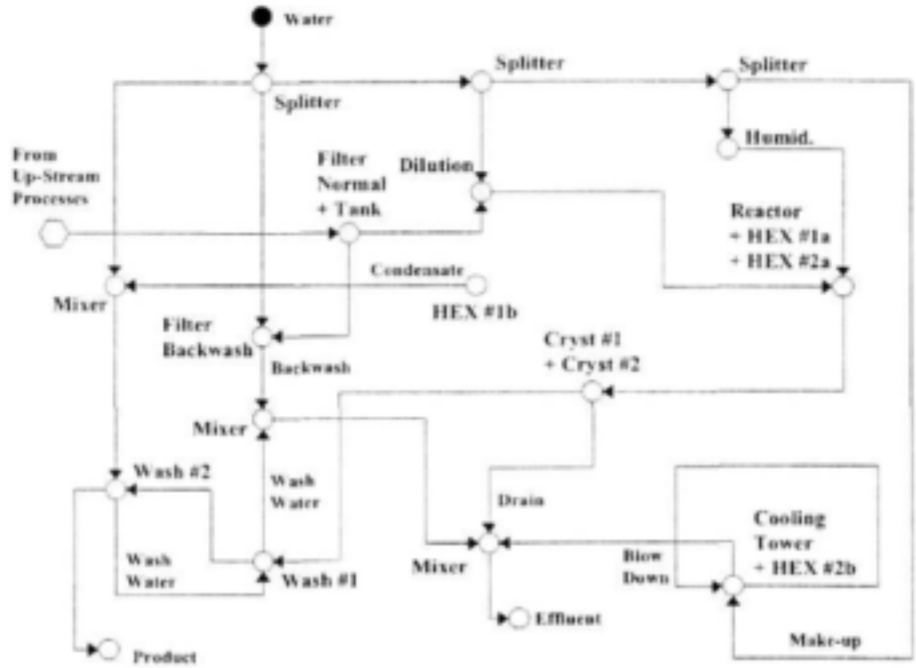


Figure 3.4: *Nodal diagram of hypothetical process following step vi).*

vii) Separate all effluent streams that are currently mixed explicitly or enter a common drainage system but not any stream that is reused within the existing process network. It may be the case that some level of water-reuse already takes place in the existing process network e.g. condensate (an effluent) being recycled back to the process instead of additional freshwater usage or a single supply of water being used for contaminant removal in multiple operations. These are features of the existing process and may not utilise the water to its full potential. These features will be dealt with in stage xi) and are left until then.

In terms of the hypothetical example, the effluent streams from the combined crystalliser, cooling tower blow down, filter backwash and wash water emerging from Wash #1 are separated.

viii) Separate all water streams coming from the same source - good quality water may be being supplied to operations when it is not needed. Each water demand is shown to be satisfied by its own independent source of water following this stage.

ix) Group operations involving process streams together such that all operation groupings fall into the categories of functional operations, functional demands and functional supplies. Do not overlap functional groupings. In Figure 3.5, the filter backwash stage is grouped together with the normal filter/tank grouping; the humidification operation is grouped with the reactor/heat exchanger grouping; the cooling circuit is grouped with the cooling tower grouping. The resulting nodal representation is presented in Figure 3.5.

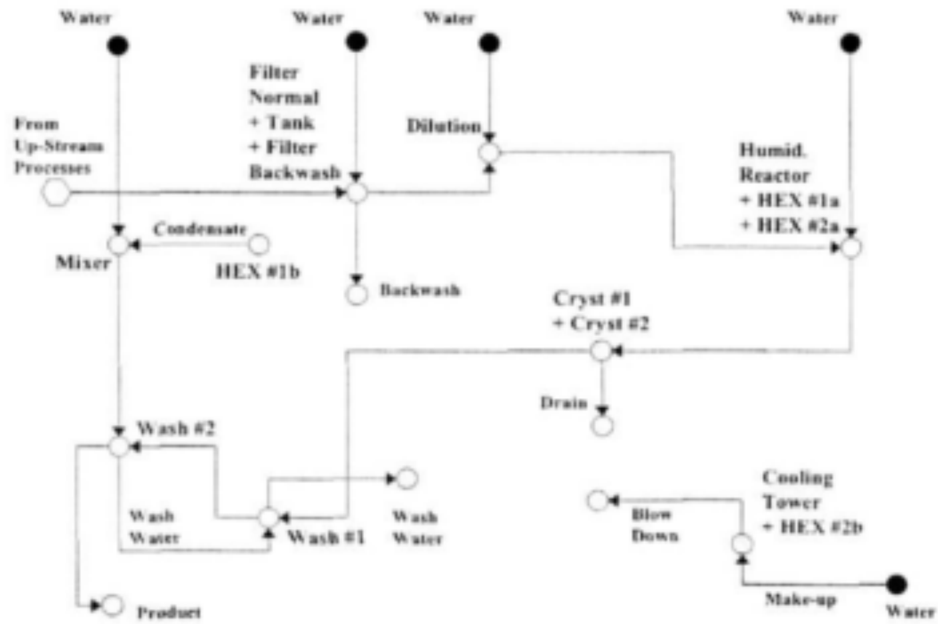


Figure 3.5: *Nodal diagram of hypothetical process following step ix).*

The simplified network obtained by the application of the above principles can now be used to guide the data acquisition stage of the study. These data are reconciled to produce a consistent data set from which the final problem is formulated.

x) Resolve the contaminant concentration differences over the functional operations into contaminant mass load additions or removals. In Figure 3.5, a mass load is transferred to the filter operation grouping and the two washing operations and a mass load is transferred to the crystalliser operation grouping (contaminated supply).

xi) Remove features of the existing process network. Condensate currently reused in the process should be represented as a supply of water available to the rest of the process; the point at which this condensate enters the existing process is represented as a water demand. A similar approach is adopted for a single water stream used for the removal of contaminants in multiple operations. Both of these cases are present in the hypothetical example (Figure 3.5). The final nodal diagram for the hypothetical pinch problem is represented in Figure 3.6.

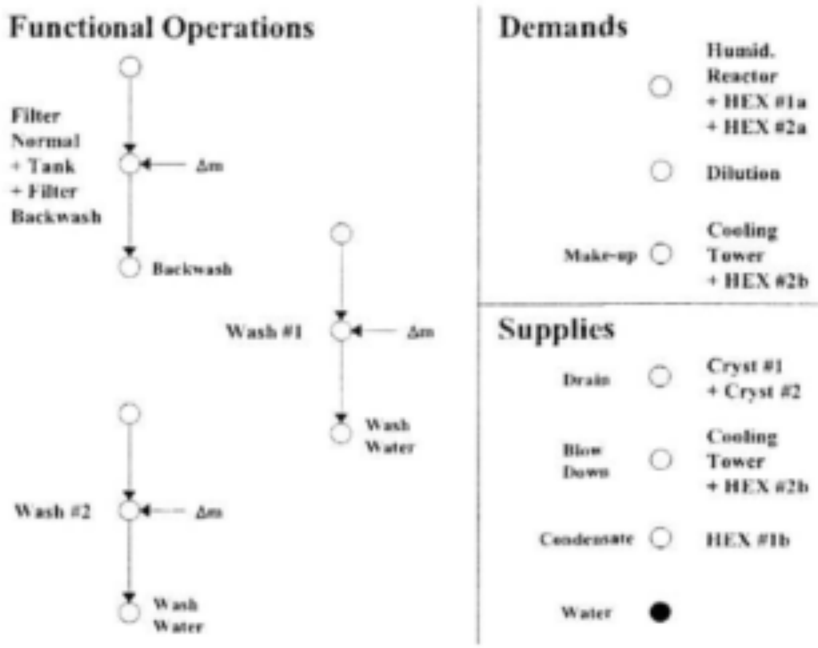


Figure 3.6: *Final nodal diagram for hypothetical pinch problem.*

3.5.3 Contaminants

It is unlikely that all the required contaminant concentration data will be readily available on the plant. In practice, certain essential determinants will be monitored at critical points in the system for process control purposes. What is sufficient for controlling a specific configuration of the process will probably be inadequate to predict what will happen when the configuration is changed.

Overcoming this obstacle usually requires the collection of samples or the use of design data. In terms of the collection of samples, it must be considered that each sample collected will have to be analysed in some form. This is usually where it becomes important to know specifically which areas of the system need to be sampled (which can be determined from the network reduction exercise) - indiscriminate and unnecessary sampling is firstly expensive and secondly troublesome and annoying for in-house personnel involved in the analyses of the samples. Where appropriate, the simplest indicator should be also chosen - for example, if a simple TDS analyses will be acceptable for the purposes of the pinch investigation, there is no reason to request detailed speciated analysis.

Another point of consideration regarding the accumulation of contaminant concentration data surrounds the degree of redundant data collected. Consider a simple process involving two inlet streams and a single outlet stream. Collecting data for two of the three streams will allow the third to be determined by mass balance. Collecting data for all three streams will result in the system being over-determined, and a reconciliation of data will be required to determine the best data for the model to represent the process. While the collection of data for the third stream does improve the reliability of the model it is not essential - this should be taken into consideration when chemical analyses are requested.

A word of caution should be issued regarding the period between sampling and sample analysis. An effort should be made to understand what is likely to happen if the sample is left to stand for any length of time. Frequently, the operating temperature and conditions from where the sample is taken are different to those in the laboratory. These factors should be taken into account when phenomena such precipitation or oxidation are likely to occur if the sample is left to stand.

3.5.4 Sources of Data

Once the significant processes and their inter-process connectivity have been established, the water mass flow rates must be determined. The are several sources for flow data:

1) Existing plant records. This is the most obvious source. Sophisticated facilities may have computerised monitoring of process flows throughout the plant.
2) **Design data**. Where available and still reasonably relevant, the original design figures can be used to estimate missing data. However, of all the aspects of a process, the water systems are perhaps the most likely to be altered as circumstances change.
3) **Control data**. There are several types of control settings that may be of interest, two are mentioned here:
   - *Ratio control*: Flows of inter-process streams dependent on others will have a corresponding control valve setting. For example, the mass flow of dilution water required for dilution of reactor feed may be dependent on the flow rate of raw materials.
   - *Composition*: Valve settings that respond to changes in stream composition or density. For example, the mass flow of steam to an evaporator may be dependent on the density of the inflow.
4) **Unit operation data**. Plant operations can offer a wealth of various types of flow rate data and relationships:
   -*Through flow*: The typical flow rate that the operation is designed to handle may be used;
   - *Flow relationships*: Design relationships between outlet and inlet flow rates may be useful, such as splitting fractions of inlet streams;
   Flow losses: Some losses are inherent to the process and must be taken into account such as leaks, evaporation rates, overflows, etc.
5) **Manual measurements.** Many smaller streams or non-process streams may not be monitored. Sometimes these streams cannot be inferred from mass balance calculations. Although not as accurate as plant records, manually measuring streams where data are not available can provide an indication of typical stream flows if several measurements are taken over a representative time interval. Manual measuring techniques range from the simple bucket-and-timer methods (or timing tank levels) to more sophisticated portable magnetic flow meters.
6) **Personal communication**. Plant personnel experienced with plant operating conditions can provide estimates of relevant flows, when other data are not available. This is the least reliable form of data, but can provide a quick insight into relative flow rates.

3.5.5 Data Reconciliation

It is usual that a set of flow and concentration data taken from a plant will be incomplete, in that measurements of flow and composition will not be obtained for every stream. It is also not necessary to measure everything, as material balances can be used to infer missing data. Conversely, some degree of redundancy will usually be present in the data set collected for a particular system, in that measurements exist for some data which could also be estimated from material balances. Since all measurements are subject to a degree of error or uncertainty, there will be inevitable discrepancies between the redundant measurements. Data reconciliation is the procedure whereby the best consistent set of data is found to represent the system. The usual method involves calculating an adjusted set of flow rates and concentrations which conform to steady-state material balances, and which are as close as possible to the set of measurements, using a constrained optimisation technique. In this procedure, measurements or estimates which are considered more reliable can be given more weight than those that have greater uncertainty. The procedure will simultaneously provide values for the unmeasured data that can be calculated by material balance. The Linnhoff-March WaterTarget™ software contains a data reconciliation module, WaterTracker™, with a number of special features for analysing incomplete data sets, which are designed to assist the data gathering process.

In applying the technique, one must be particularly aware of the implications of steady state assumption. In most cases, the pinch analysis will involve a steady state model of the process, so it is appropriate for the data conciliation to use steady state balances. However, a chemical plant is a dynamic system and plant measurements taken at a particular moment are subject to the conditions prevailing at the time e.g. load, type of feed stock, *etc*. Since the collection of data will usually be done over a period of weeks in which conditions of operation vary, it is unlikely that the measurements will reflect steady operating conditions. It may even happen that, during this time, changes might be effected to the plant which, although not largely significant on their own, will be significant enough to make the supposedly best set of data, as determined through data reconciliation, not as representative as initially intended.

3.6 Modelling of Unit Operations

Because of the complexity of the optimisation procedures, it is desirable that the modelling of the individual processes should be as simple as possible, while still representing the essential behaviour of the system over the range of conditions that will be considered in the optimisation process. The approach usually taken is to formulate material balances for the various units, with certain coefficients derived from plant records, which substitute for the equilibrium and kinetic relationships which would be required in a more fundamental model. Furthermore, since the optimisation is concerned with altering operating conditions, those parts of the system which may not be altered need not be modelled explicitly.

Many water using processes can be represented by the very simple mass pickup model proposed by Wang and Smith (1994a) (see **Section 2.2**, figure 2.1), or by a combination of two or more such models. However, occasions arise where it is not possible to represent the behaviour of a unit operation in this way, and special models have to be constructed. The Lethabo Power Station study includes examples of special models for a Reverse Osmosis plant and an Ion Exchange plant (**Section 6.1.3**). The Linnhoff-March WaterTarget™ software includes several special built-in models, and a facility for constructing new ones, within certain mathematical limitations.

3.7 Optimisation

Water pinch analysis is essentially based on optimisation techniques: this applies to all its forms, including the graphical methods. The problem is formulated as a *constrained optimisation*, in which the objective function to be minimised is related to the costs associated with water use, and the constraints to be met are related to the material balances and process requirements that arise from the technologies under consideration. In such a formulation, when the optimum configuration is found, some of the inequality constraints will be *active*, i.e. directly preventing any further improvement in the objective function, and others will be *inactive*. The *pinch* is an abstract concept that refers to the set of active constraints. *Pinch analysis* refers to the investigative and design methods which try to identify the pinch and design systems which explicitly take it into account.

Once the optimisation problem has been mathematically formulated, there are very many techniques available to seek the optimum solution. However, there are none known which are universally effective, each has a particular class of problems that is best suited for.

3.7.1 Constraints

The types of constraints encountered in the design of water reuse networks are presented below:

Mass Balance Constraints

These equality constraints are used to describe the relationships that exist between flows, contaminants and contaminant mass loads over operations and between operations.

Flow Constraints

These constraints control the flow into and out of operations and also between operations. Maximum flows and minimum flows into, out of and between operations are described by "less than" and "greater than" (inequality) expressions respectively. Flows into, out of and between operations may be set by equality constraints.

Concentration Constraints

These are inequality ("less than") constraints which are used to limit the contaminant level entering or leaving an operation.

Logical Constraints

These constraints are inequality constraints involving logical variables and are used to control various structural characteristics of the water-reuse network. They may be applied to ensure that if a quantity of water is supplied between two operations, the quantity is greater than a certain value (thereby preventing small volume connections being made). A further use of these constraints is to prevent direct and indirect recycles in the reuse network.

Within WaterPinch™ these constraints may be introduced into the problem in a tabular format. Mass balance relationships are expressed through the inclusion of the various process models available in the software. In both cases, an actual knowledge of the mathematical structure of the constraint is not required.

3.7.2 Objective Function

To complete the optimisation problem formulation, an objective function must be chosen. In the first papers that introduced water pinch analysis, the objective function was simply the total fresh water used by the system, to be minimised. By mass balance, this results in effluent generation being minimised at the same time. The simplicity of the objective is what allows the use of the graphical methods of solution. However, this approach is usually too simplistic in practice. As a simple example, in a system with a treatment process that regenerates effluent to a quality that allows it to be reused, the cost of the treatment must also be taken into account: optimising in terms of fresh water use alone could lead to an absurd result. Where a pinch analysis is applied to an existing plant, the situation is complicated by the cost of changing the system, or conversely by the benefit of retaining as much of the existing system as possible.

Mathematically, the objective function has to be formulated in terms of the decision variables, i.e. those variables which are free to be manipulated. Typically these are the water flows between the unit operations in the system. This can lead to difficulties with representing the engineering investment costs of installing equipment, which are not obviously related to flow rates. This is the standard issue of fixed and variable costs in engineering design, and there are several standard methods of dealing with it (see e.g. Biegler *et al.*, 1997, **Chapter 5**).

The objective function used need not constitute a full costing of a process. Costs which will not change as a result of the changes allowed to the pinch model can be left out. Thus, in the Lethabo investigation, lime softening contributed a significant proportion to the running costs of the water system, however this was fixed by the carbon dioxide absorbed in the cooling towers, which would not be altered by any changes to the way the units in the circuit were interconnected.

Conversely, the objective function might include terms which were not strictly financial costs, in order to represent goals which are extra-economic. Environmental or social goals are an obvious example; however these raise difficult problems of how to express them on a common basis with normal financial costs. Once again, the Lethabo Power Station investigation serves as an example, in that it attempted to incorporate the cost of discharging salt to the environment.

3.7.3 Solution Techniques

Once the pinch problem has been formulated, a number of techniques are available which can be used to solve the problem. These techniques may be divided into three categories - heuristic procedures, graphical methods and mathematical programming techniques. The hierarchy of solution methods is as follows: heuristic procedures, graphical methods and mathematical programming techniques. Heuristic procedures and graphical methods offer the advantage that they do not require specialised computer software packages or computer programming. The techniques are however unlikely to produce the optimal water management solution when it comes to larger problems involving multiple contaminants. In addition, the economic aspects of the problem, which is usually the criteria against which the pinch problem is to be optimised, cannot be dealt with in much detail resulting in solutions which appear good from a water-reuse perspective, but are costly to implement. Mathematical programming techniques offer greater flexibility in terms of problem size, number of contaminants and economic analysis of the problem, but these techniques are generally only accessible through computer packages which are often expensive and require some experience in order to use. The benefits of these packages are however that the water reuse strategy produced is more likely to be economically viable. A brief description of the different techniques is presented below:

Heuristic Techniques

These procedures are based on rules of thumb rather than a formalised approach - see Liu 1999 (Liu 1999). No experience was gained with use of these techniques during this project.

Graphical Methods

Two methods are prominent: the approach initiated by Wang and Smith (1994a, 1994b, 1995a) and that proposed by Beuhner and Rossiter (1996). The Wang and Smith method is generally suited to simple systems involving single contaminant mass-exchange type operations. The technique has been extended to deal with multiple contaminants but the procedure becomes increasingly cumbersome for greater numbers of contaminants. The technique also breaks down when no mass-exchange operations are present in the system.

The method proposed by Beuhner and Rossiter is more general in terms of the types of operations that can be handled, but the technique is still best suited to single contaminant problems. In addition, because of the nature of the supply and demand composite curves, some degree of abstraction is introduced in that the link between process inlet and process outlet is removed. For example, the inlet demand and the outlet supply from a mass-exchange type operation will be represented independently - the link between the two will have to be included externally and the graphs plotted once more.

The method of Beuhner and Rossiter has been extended to deal with reagent dilution operations with some success - this modification however only applies to the single desirable species case. The procedure is presented in **Sections 4.2** and **4.3**.

Mathematical Programming Techniques

Mathematical programming techniques are by far the most flexible when it comes to the design of water-reuse networks. The type of programming technique used for the design depends primarily on the complexity of the system under consideration. In general, a non-linear programming (NLP) formulation of the problem is required, though in some cases sequential linear programming techniques may be used. The inclusion of mixed integer (or logical) variables in the problem (resulting in a mixed integer non-linear programming (MINLP) formulation of the problem) results in the most general and complex description of the problem.

A verbal statement of the mathematical programming problem as it pertains to the design of water-reuse networks is as follows: *minimise the objective function subject to a set of constraints*. The objective function will either take the form of the amount of freshwater used or more likely the water cost (which then can include wastewater treatment costs and other costs associated with the network). Constraints are the mathematical expressions used to describe the model physically. Equality constraints describe the absolute relationships, e.g. mass balance relationships, that exist between operations while inequality constraints are used to describe other characteristics of the model such as the maximum permitted concentration into or out of a particular unit operation.

In general, mathematical programming techniques are only practicable through the use of computer packages. Some of these packages require the problem to be set up *ab initio*, while others provide building blocks and built-in process models for formulating the problem. Experience gained in this area during the course of this project is limited to MATLAB, which was used in the solution of the Lethabo Power station problem, and WaterTarget™ which was being used for the later projects. MATLAB provides a high level programming language, with *toolboxes* of specialised subroutines, in particular a non-linear constrained optimisation solver, however all the process models have to be programmed by the user.

WaterTarget™

Linnhoff-March's WaterTarget™ is a software suite used for the design of water-reuse networks. The software suite comprises two modules - WaterTracker™ and WaterPinch™ (which can be purchased separately or together). WaterTracker™ is a tool designed to assist the data gathering and reconciliation part of the investigation. The solution of the formulated water-pinch problem is then produced by WaterPinch™ module. More specifically, WaterPinch™ is a front-end tool to the solution algorithm which is written in GAMS (General Algebraic Modelling System), a mathematical programming language for the solution of mathematical programming problems. WaterPinch™ allows the problem to be formulated in a user-friendly environment and transfers the formulated problem to the solution algorithm. The results produced by the solution algorithm are then transferred back to WaterPinch™ which presents these in a report- and graphical format.

3.7.4 Convergence

Most optimisation methods use iterative algorithms: the term *convergence* describes the process of approaching the optimal solution by series of approximate estimates. Convergence properties vary with the class of problem and the algorithm. With linear problems, convergence can be guaranteed in almost all cases. Convergence is usually much more difficult with non-linear problems. Furthermore, a non-linear problem has the difficulty that it may contain both a *global optimum* and one or more *local optima*, and an algorithm may converge towards a local optimum instead of the desired global optimum. The role of the *starting estimate* is crucial: a good starting estimate will lead to convergence to the global optimum.

The main practical issue arising out of these considerations is the need to check any solution achieved by an optimisation algorithm to establish whether it corresponds to the global optimum. The problem with this is that the only way to guarantee that a particular point is the global optimum is to do an exhaustive search of the *feasible region* (i.e. the set of all combinations of variables which satisfy the constraint relationships). To carry this out is usually impractical. A more realistic strategy is to try a number of different starting estimates, and to see whether the algorithm converges to the same solution; if not, to choose the best one encountered. In the case of an existing plant, choosing the current situation as the starting estimate has the advantage that any better solution must at least represent an improvement on the current practice.

3.7.5 Sensitivity Analysis

Once a mathematical solution has been obtained for the optimisation problem, it is necessary to evaluate how well the solution corresponds to the physical system it is supposed to represent. Clearly, in view of all the approximations and simplifications involved in pinch modelling, the correspondence will never be complete. Sensitivity analysis, which involves checking the sensitivity of the model to key assumptions and coefficient values, is a valuable general technique for establishing the validity of a model. In pinch analysis it has a special key role, in that the pinch can be viewed as the set of limiting constraints on the system, so that pinch analysis can be considered as a special case of sensitivity analysis. Thus, the Linnhoff-March WaterPinch™ software provides tools for examining the sensitivity of the solution to the critical concentration constraints, and treats this process as central to the pinch analysis. These take the form of a sensitivity coefficients for each limiting constraint. The sensitivity coefficient is defined as the gradient of the cost objective function with respect to a change in the concentration constraint in question, assuming that all other factors in the model remain fixed.

In most cases the investigator must go even further. In the first instance, the sensitivity coefficient is only guaranteed to apply over an infinitesimal change from the calculated optimum solution. As the limit is relaxed, the solution may encounter another constraint which becomes limiting. Secondly, is may be important to investigate coefficients and constraints other than the concentration limits, since the pinch model will probably be multidimensional, involving uncertainties in factors other than just concentrations. As an example, in the Lethabo Power Station investigation, in order to prevent the discharge of salts to the environment, an environmental cost coefficient had to be introduced, which forced the reverse osmosis plant to be used. The estimated value of this coefficient was subject to considerable uncertainty, and so it was necessary to establish the sensitivity of the model to this value.

3.7.6 Scenarios

In undertaking a comprehensive sensitivity analysis of the pinch model, there may be too many factors involved for it to be practical to investigate them all. It is also usually the case that the model will be completely insensitive to many of them. If it were known in advance which these were, the task could be made more manageable by eliminating them from the sensitivity analysis. A practical approach to the difficulty is to use engineering intuition to construct a number of scenarios to investigate, in which variables that are expected to have a strong effect on the model, and which are subject to significant uncertainty, are varied. The Lethabo investigation once again provides and example, where two scenarios were presented in which the separation performance and operating costs of two different RO plants were used, based on two actual plants operated at different power stations.

3.7.7 Significance of Results

The preceding paragraphs should have made it clear that the results yielded by a pinch analysis often have to be interpreted with great care, taking into account modelling uncertainties and assumptions, together with practical engineering insight into the physical processes involved. This will be particularly important where the optimum plant configuration determined from the pinch analysis differs substantially from the existing configuration, because contaminants which where not considered in the model might become limiting in the new configuration. Assessing the results of the analysis should be a consultative process between the modeller, who understands the assumptions of the model, and plant personnel who understand the realities of their processes.

4 THE SASOL POLYMERS CHLOR-ALKALI PLANT

The initial study was carried out during 1997 by Grant Gardner, and form the basis of his MScEng thesis (Gardner, 2000), which provides a more detailed account of the material of this chapter . At this time we had not fully appreciated the issues of distinguishing between process water streams and utility water streams, nor had we found a systematic way of dealing with multiple contaminants or solutes. The methods found to address these problems were very specific to the process in question. The key issue was the presence of hydrochloric acid (HCl) and sodium hydroxide (NaOH) in the system.

4.1 Process Description

The following sections briefly describe the processes on the site, as they were configured at the time (1997). The relationship between the plants is illustrated in Figure 4.1.

Figure 4.1: *The chlor-alkali and related processes at the Sasol Polymers plant, Umbogintwini.*

4.1.1 Brine Circuit

A 22 % m/m solution of sodium chloride circulated through the membrane plant, at the exit of the cells the brine had a pH of 4. The pH of the brine was lowered to 2 by in-line injection of 31 % m/m HCl. The acidified brine was then passed through a series of dechlorinators and dechlorinated to 6 ppm (as chlorine). The chlorine-contaminated air was then fed into the weak chlorine main. The dechlorinated brine was then fed into a brine return tank, where the pH was raised to 8.5 using a sodium hydroxide solution with a density of 1 200 kg/m^3 (18.5 % m/m at 25 °C).

The alkali brine was then passed to a set of resaturators where the concentration of NaCl was controlled to 26 % m/m by the addition of salt and process water as required. At this point several impurities were introduced, the most notable were calcium, magnesium and sulphates. The sulphates did not cause a serious problem, but could build up to problematic levels in the circuit if not occasionally purged.

The 26 % m/m brine solution was then fed to a calcium reactor where the calcium ions were precipitated out of solution as calcium carbonate by the addition of a sodium carbonate solution with a density of 1 110 kg/m^3 (10.9 % m/m at 25°C). The pH of the brine was then raised to 10 by the addition of sodium hydroxide (18.51 % m/m) in the magnesium reactor in order to precipitate the magnesium ions as magnesium hydroxide.

A flocculant (Anikem) was added to the brine prior to it being pumped to the clarifiers, where the $CaCO_3$ and $Mg(OH)_2$ precipitates were allowed to settle, and were continuously drawn off as sludge. This sludge was then disposed of by Wastetech. The clarified brine was then drawn through filters to remove any solid carry over. The filters were routinely back washed using brine. The backwash then passed into a brine recovery tank, re-entering the system before the clarifiers.

4.1.2 Chlor-Alkali Membrane Plant

After leaving the filter on the brine plant the 26 % m/m brine solution was pumped to the membrane plant. Here the brine was chemically dechlorinated and α-cellulose is added before the brine is polished in the polishing filter to remove any trace of heavy metals. After polishing the brine flowed into a holding tank and then onto a secondary purification stage. The brine was then passed though two cation exchange columns in series to purify it. The purified brine was stored in a head tank before being passed to the membrane cells as the anolyte. Migration of sodium ions occurred through the membranes into the catholyte. The catholyte was a 30 % m/m solution of sodium hydroxide that was concentrated to 32 % m/m by the migration of the sodium ions and the subsequent reaction of these ions with water to form sodium hydroxide and hydrogen.

The catholyte then passed through a hydrogen separation unit before part of it was sent to a series of concentrators, where it was concentrated to saleable sodium hydroxide (48 % m/m). The remaining 32 % m/m sodium hydroxide was diluted with demineralised water and became the circulating catholyte.

The hydrogen was cooled before being sent to storage and was distributed as a feed stock to ALLIANCE PEROXIDE and the hydrochloric acid plant for the manufacture of hydrogen peroxide or hydrochloric acid. Chlorine was formed on the anolyte side of the membranes, the chlorine and the lean anolyte underwent a natural separation (gas and liquid). The chlorine was cooled before it was sent to the chlorine processing plant. The lean anolyte was then passed to the lean brine tank, dechlorinated and treated with sodium bisulphite before being returned to the brine circuit.

4.1.3 Chlorine Processing

Apart from producing liquid chlorine, the chlorine processing plant consisted of several smaller plants, namely the Cereclor, Sodium Hypochlorite, the Hydrochloric Acid and the Solvents Plants.

4.1.3.1 Liquid Chlorine Plant

Chlorine gas from the cell room flowed into the chlorine processing plant where it was cooled and the excess water knocked out by passing it counter currently to circulating water in a cooling tower. The circulating water passed through a water-cooled heat exchanger before re-entering the cooling tower. The water overflow from the cooling tower passed through air dechlorinators with the chlorine contaminated air being vented into the *weak main*. The overflow water was then pumped to a holding tank before being pumped to the hypochlorite plant, where it was used as makeup water for the sodium hydroxide dilution.

The wet chlorine then flowed through a wet candle filter where any solids and a small amount of water was knocked out. The knocked out water was then mixed with the cooling tower overflow. The chlorine gas was then dried with 98 % m/m sulphuric acid in three drying towers. The spent sulphuric acid was dechlorinated before being sent to KYNOCHEM. The chlorine was then compressed, and some of it turned into liquid chlorine by means of refrigeration system. It was then distributed to customers in road tankers, 1 000 kg drums and 70 kg cylinders. The liquid chlorine was stored on the plant.

Some of the liquid chlorine was vaporised and used as a gas feed for the manufacture of Cereclor. The remainder of the chlorine gas (the part which was not liquefied, known as chlorine tail gas) passed either to the Solvents Plant, the Hydrochloric Acid Plant or the Sodium Hypochlorite Plant as chlorine feed.

4.1.3.2 Cereclor

Cereclor was produced by the reaction of chlorine gas with a high purity straight chain paraffin in batch reactors at 105 °C, with the evolution of HCl gas. Liquid chlorine was vaporised using steam and then introduced to the reactor via a sparge ring, and the temperature of the exothermic reaction is maintained at 105°C by passing cooling water through the reactor jacket and a monel coil.

The HCl was withdrawn from the top of the reactor. It passed through a catch pot with de-mister to remove entrained n-paraffin before it entered a carbon block absorber/scrubber, where it was absorbed into process water. This produced a 31% industrial grade hydrochloric acid. The hydrochloric acid was sold in bulk.

The chlorination of the n-paraffin continued until the desired end-point density was reached. The chlorine flow was then stopped and dried filtered air was introduced to remove unreacted chlorine and traces of HCl. The gases leaving the carbon block scrubber were vented to the weak chlorine main. Once air blowing was completed, an epoxidised soya bean oil stabiliser was added and the batch pumped to stock.

4.1.3.3 Sodium Hypochlorite

The Sodium Hypochlorite Plant produced sodium hypochlorite from sodium hydroxide, and all the weak chlorine gas vented from the Brine Plant, Membrane Plant and Chlorine Processing Plant. This plant ensured that no chlorine gas escapes to the atmosphere.

The sodium hypochlorite plant had two main functions:

1) to act as a reliable sink for chlorine-containing vent gasses, both for normal routine operational vents and emergency venting; and
2) to produce sodium hypochlorite of saleable quality from as much of the chlorine which entered the Sodium Hypochlorite Plant as possible.

The sodium hypochlorite plant consisted of five primary absorption towers. The primary towers were for hypochlorite production. The secondary absorption section comprises of one backup tower in series with the primary towers. The secondary absorption section acts purely as an ultra reliable standby chlorine sink.

In the sodium hydroxide mixing tank an 8 m^3 batch of 22 % m/m sodium hydroxide was made up by the dilution of 32 % m/m sodium hydroxide with process water while being agitated with air. The 22 % m/m solution was pumped to a circulating tank; the sodium hydroxide was then circulated over the absorption tower, which drew suction from the weak main (typically 1 % m/m chlorine). The liquor leaving the tower passed through a water-cooled heat exchanger before being returned to the circulating tank. This was continued until the batch was complete. A completed batch of sodium hypochlorite contained approximately 15 % m/m [18 % m/v] available chlorine.

4.1.3.4 Hydrochloric Acid (HCl)

HCl was made by burning chlorine tail gas and hydrogen in a carbon block Hydrochloric Acid Synthesis Unit. The chlorine was burnt in an excess of hydrogen, in the carbon combustion chamber at the base of the unit.

The hydrogen chloride gas and any unreacted hydrogen passed up the unit through the carbon block absorber and scrubber sections. Water was added at the top of the scrubber section and passed down the unit counter currently to the HCl. The HCl was absorbed in the water to produce 31 % HCl, which was drawn off the unit above the combustion chamber, and the unburned hydrogen left via the vent at the top of the unit. This then passed through a scrubber where the unburned gas was scrubbed with a weak circulating sodium hydroxide to remove any chlorine and hydrochloric acid before being vented to the atmosphere.

Chemically pure hydrochloric acid was made by reducing the chlorine flow and increasing the hydrogen ratio so that the acid produced had low free chlorine. Demineralised water was used for absorption of the hydrogen chloride. Any iron in the acid was removed by circulating the acid produced through an iron-specific ion exchange resin.

4.1.3.5 Solvents

Trichloroethylene, a chlorinated solvent, was produced in a three-stage process. Acetylene and chlorine tail gases were reacted at an elevated temperature in a stirred cooled monel reactor that operated full of tetrachloroethane.

The reaction was catalysed by ferric chloride, which was added as iron powder. The tetrachloroethane overflowed to stock via a catch pot in which the solid catalyst was removed. The vent gases from the tetrachloroethane reaction passed into a water-cooled condenser where the trichloroethylene and tetrachloroethane vapour were condensed and sent to the *heavies recovery tank*. The remaining gases flowed through a series of scrubbers where they were scrubbed with a 1 % m/m sodium hydroxide solution in order to remove any chlorine before venting to the atmosphere. The aqueous effluent from the scrubbers flowed to the *Hydecat Unit* where the destruction of any sodium hypochlorite took place. The tetrachloroethane was pumped continuously from the tetrachloroethane stock tanks into two cast iron converters, where the tetrachloroethane was dehydrochlorinated to form crude trichloroethylene. This was achieved by reaction of the tetrachloroethane with lime slurry (calcium hydroxide) at 95 °C. The lime slurry was a by-product of acetylene generation.

The crude trichloroethylene formed boiled off and was condensed in a water-cooled condenser. The crude trichloroethylene then passed through the first water separator where the excess water was removed. The crude trichloroethylene then passed through the first set of calcium chloride dryers and ran to the crude trichloroethylene stock tanks. The crude trichloroethylene was purified by continuous distillation. The overhead product of the distillation process was washed with process water and passed through dryers where it was dried with calcium chloride before being run to product stock tank. The trichloroethylene heavies were continuously removed, and transferred to the crude tetrachloroethane stock tanks for return to the converters with the tetrachloroethane feed.

4.1.3.6 Acetylene generation

Calcium carbide was reacted with water in an acetylene generator to produce acetylene gas and a lime slurry by-product.

The acetylene gas was then compressed and dried before being piped to the Solvents and VCA Plant. The calcium hydroxide slurry was pumped to the slurry pits before being pumped to the Solvents Plant where it was used in the dechlorination of tetrachloroethane in the converters. Acetylene production was 4 500 m^3/day.

4.1.3.7 Vinyl Chloroacetate

Monachloroacetic acid reacted with acetylene to form vinyl chloroacetate in a batch reactor. Mercuric oxide was used as a catalyst and hydroquinone was used as an inhibitor against polymerisation.

After reaction the vinyl chloroacetate was vacuum distilled to a purity better than 95 %, and inhibited with methyl ether of hydroquinone [MEHQ]. At the end of the distillation, the reactor heel was drummed and the top organic layer is recycled back to the reactor. The bottom sludge was disposed of by encapsulation in concrete. All the vapours generated by the process were removed through a ventilation system and scrubbed with a circulating 15 % m/m sodium hydroxide solution in a scrubber.

4.1.3.8 Hydecat Plant

Effluents containing free chlorine, mainly the Solvents Vent Scrubbers effluents and off-specification sodium hypochlorite product, were pumped to holding tanks on the Hydecat Plant. Here the vent scrubber effluent was used to dilute the off-specification sodium hypochlorite product, such that the feed to the Hydecat reactor contained less than 3 % m/m sodium hypochlorite. The Hydecat reactor consisted of two beds packed with the nickel-containing Hydecat catalyst. The level of free chlorine in the reactor feed was reduced to 10 ppm. The outlet stream was then sent to drain as an effluent.

4.2 Theoretical Issues

The reactivity of the HCl and NaOH species present in the system introduced a further dimension to the problem of water minimisation. They are expensive relative to water, so it is important to use them efficiently. This means that the situation presented by the complex is one in which the optimal solution relative to cost is most unlikely to coincide with the one featuring the lowest water consumption and effluent generation. A further significant feature was the presence of a number of dilution-type operations on the complex. These operations involve the dilution of either concentrated NaOH or concentrated HCl acid with fresh water such that a stream or intermediate strength is produced. Three utilisation patterns for the diluted reagent stream were identified: it could be used to manufacture a product, it could be sent directly to the effluent handling 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 handling facility. As such, the reagent containing streams from the last two situations could be recovered by using them for dilution purposes instead of freshwater; this practice would result in savings in concentrated reagent and water utilisation and effluent production.

In practice, dilution operations are required on an industrial plant to bring the purchased and concentrated reagent 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 comprises a particular mass of reagent species and a particular mass of water, both of which are significant and set by the process requirements. The concentrated reagent similarly comprises a reagent fraction and a water fraction. Where only freshwater and concentrated reagent are used to produce the dilute stream, the water balance comprises contributions from both the fresh water stream and the concentrated reagent stream; the reagent balance is however satisfied completely by the concentrated reagent source. Where a reagent containing effluent is used for dilution purposes, both the water and reagent balances are satisfied by contributions from both the effluent and concentrated reagent sources. As a consequence of the effluent's contribution to the reagent species balance, a smaller quantity of concentrated reagent is required by the operation. However, in order to meet the fixed flow rate requirement of the dilution operation, an additional amount of water must be added using either fresh water or additional reagent containing effluent.

Hence, 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 operation, but an increase in the amount of water supplied either through fresh water or reagent containing effluent. Diluting the concentrated reagent using only fresh water corresponds to the lowest volume of water but the greatest amount of concentrated reagent. Conversely, the lowest requirement for the concentrated reagent occurs when the reagent containing effluent is at the concentration produced by the dilution operation. Thus in effect, the amount of water required for dilution purposes is dependent on the level of reagent present in the diluting stream.

In identifying an approach to targeting the optimal water and reagent management strategy for the complex, it must be recognised that most of the operations within the complex do not fall into the mass-exchange category. For this reason the use of the Wang and Smith approach (Wang and Smith, 1994a) and that proposed by El-Halwagi and Manousiouthakis (1989a) are not directly applicable. The reactivity issue, associated with the presence of HCl and NaOH, is circumvented by dividing 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. This decomposition strategy allows each sub-problem to be approached from a single contaminant perspective, which can be justified since the HCl concentration limit for an NaOH tolerant operation would be zero and vice versa. A further simplification is made by excluding from the analysis those streams for which the flow rate falls below a particular threshold value. This simplification is justified on the basis that it is economically impractical to recover these streams.

The approach adopted in addressing the problem presented by the 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 is able to accept water of a quality up to the reagent concentration produced by that operation; this assumption is aimed at promoting the recovery of reagent containing effluents, which in turn represents the most effective total cost strategy. Since the water demand for the operation is dependent on the concentration of reagent present in the diluting effluent, the targeting procedure requires an iterative calculation.

4.3 Calculation Procedure

The procedure is best illustrated by example. The data in Table 4.1 were obtained from the subsystem at Polifin involving NaOH tolerant streams and operations .

Table 4.1: *Data for the NaOH subsystem of the Sasol Polymers Chlor-Alkali Process.*

Process Number	Total Flow [kg/h]	NaOH Conc. [ppm]
	Demands	
3	2 476.27	220 000
4	2 467.50	185 131
5	498.44	185 131
6	701.16	19 057
8	335.92	13 129
1	3 769.46	10 000
	Sources	
2	4 093.69	8 941
7	689.38	2 300
9	332.03	1 575

Step 1

Each reagent source and demand operation is characterised by the mass of reagent species and the mass of water required or available. Initially it is assumed that only fresh water is used as the diluting agent for each reagent dilution operation. The amount of fresh water required by each reagent dilution operation is determined by subtracting the amount of water accompanying the concentrated reagent source from the total mass of water in the outlet stream (Table 4.2). The supply concentration of the concentrated reagent is 320 000 ppm. The amount of water accompanying the reagent containing effluents is presented in Table 4.3.

Table 4.2: The freshwater requirement for the reagent demands from Table 4.1

Process Number	Total Flow [kg/h]	Conc. [ppm]	Reagent Mass [kg/h]	Water Mass [kg/h]	Water from Reagent [kg/h]	Freshwater Demand [kg/h]
			Demands			
3	2 476.27	220 000	544.78	1 931.49	1 157.66	773.83
4	2 467.50	185 131	456.81	2 010.69	970.72	1 039.97
5	498.44	185 131	92.28	406.16	196.10	210.06
6	701.16	19 057	13.36	687.80	28.39	659.41
8	335.92	13 129	4.41	331.51	9.37	322.14
1	3 769.46	10 000	37.69	3 731.77	80.09	3 651.68

Table 4.3: The water supply available from reagent containing effluent sources

Process Number	Total Flow [kg/h]	Conc. [ppm]	Reagent Mass [kg/h]	Water Mass [kg/h]	Water Supply Flow [kg/h]
			Sources		
2	4 093.69	8 941	36.60	4 057.09	4 057.09
7	689.38	2 300	1.59	687.79	687.79
9	332.03	1 575	0.52	331.51	331.51

Step 2

The source and demand composite curves are plotted on axes of concentration versus water flow rate (Figure 4.1). The demands are characterised by the flow rate of water determined in *Step 1*, and the concentration of the reagent in the outlet stream of the dilution operation. The sources are characterised by the water flow rate determined in *Step 1*.

Step 3

Vertical lines are drawn from the termination points of each operation making up the demand composite curve to create flow intervals (Figure 4.2). Water sources available within each flow interval are used to satisfy the demands with that flow interval, and the network designed accordingly.

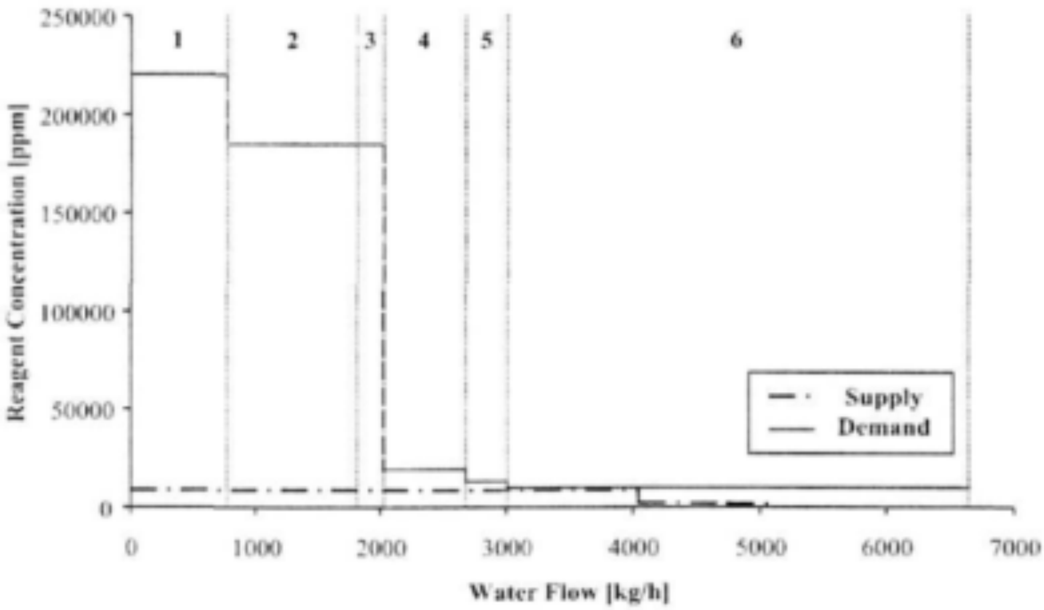


Figure 4.2: *The source and demand composite curves for the first iteration in the design of the network involving NaOH tolerant streams and operations.*

Step 4

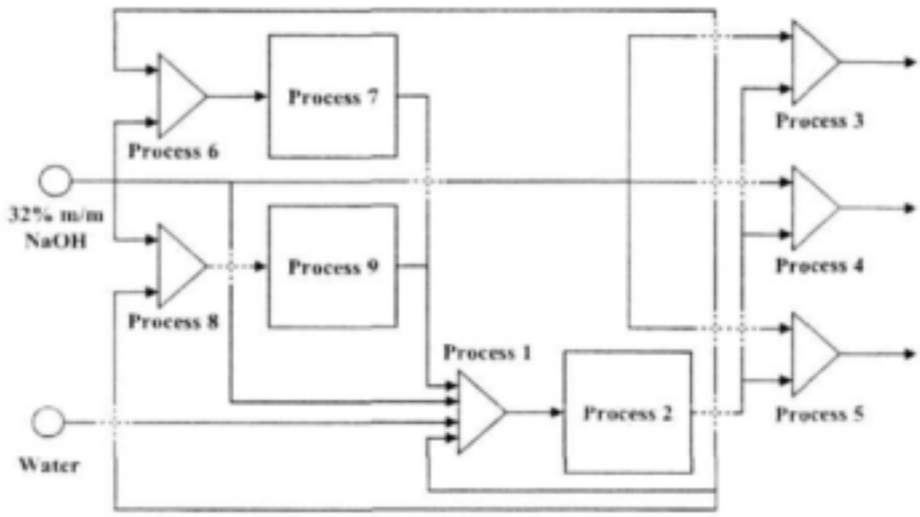
The implications of using the reagent containing effluent streams for dilution instead of freshwater are quantified in this step. The amount of concentrated reagent required by the dilution operation is determined by subtracting the mass of reagent contributed by the effluent stream from the total requirement. The amount of water required for dilution is determined by subtracting the amount of water contributed by the concentrated reagent from the total requirement for the operation.

Step 5

The source and demand composite curves are re-plotted, except in this case, the updated water demands determined in *Step 4* are used in the construction of the demand composite curve. The network is redesigned as laid out in *Step 3*. Iterations around *Step 3*, *Step 4* and *Step 5* continue until convergence.

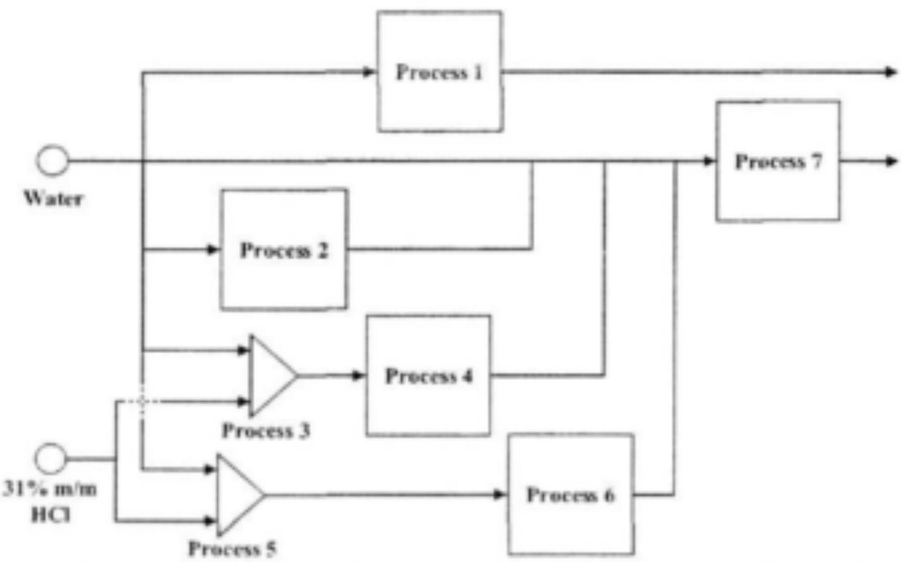
4.4 Results

Figure 4.3 shows the final network design for the NaOH using section of the process. The final network design for the HCl using operations and streams is presented in Figure 4.4 The corresponding calculation results are summarised in Table 4.4.



1 - Solvents Vent Scrubber - Dilution	6 - Demin Regeneration - Caustic Mixing
2 - Solvents Vent Scrubber	7 - Demin Regeneration
3 - Sodium Hypochlorite - Caustic Mixing	8 - Brine Circuit IOX Regeneration - Caustic Mixing
4 - Brine Circuit - pH Adjustment	9 - Brine Circuit IOX Regeneration
5 - Brine Circuit - pH Adjustment	

Figure 4.3: *Final network design for the Sasol Polymers NaOH subsystem.*



1 - HCl Synthesis	4 - Brine Circuit IOX Regeneration
2 - Stock Tank Vent Scrubber	5 - Demin Regeneration - HCl Mixing
3 - Brine Circuit IOX Regeneration - HCl Mixing	6 - Demin Regeneration
	7 - Cereclor HCl Production

Figure 4.4: *Final network design for the Sasol Polymers HCl subsystem.*

Table 4.4: *Summary of the results obtained from the initial Water Pinch Analysis study carried out at Sasol Polymers*

	Original Flow [kg/h]	**New Flow [kg/h]**	**Percentage Saving [%]**
	NaOH Network		
Water	4 785	0	100
Effluent	5 667	1 971	65
NaOH (100% m/m)	1 180	1 146	2.9
	HCl Network		
Water	763	0	100
Effluent	5 467	4 114	25
HCl (31% m/m)	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
NaOH (100% m/m)	1 180	1 146	2.9
HCl (31% m/m)	5 963	5 723	4.2

4.5 Conclusions

The chlor-alkali process uses water in a more complex role than has been addressed by standard pinch analysis theory. The most important feature of this is the presence of reagents and products such as NaOH and HCl in the water streams. The recovery and reuse of these components may be more important than the reuse of water. Furthermore, such components introduce process constraints which are quite different from those arising from contaminants.

The Two-Composite Methodology was extended to address to the simultaneous targeting of water and reagent use, although restricted to a single reagent. It was however recommended that theory pertaining to the targeting and design of networks involving reactive species be further developed to take into account the multiple contaminant nature of the problem.

The restricted nature of the method did not allow the presence of other contaminants in the system, such as calcium and magnesium, to be accounted for. The results of this study therefore have to be considered as preliminary, and further investigation is required to consider whether they might preclude any of the suggested reuse options.

5 THE SANACHEM AGRO-CHEMICALS PLANT

This investigation was the topic of Thokozani Majozi's MScEng thesis (Majozi, 1998), which contains a more detailed presentation of the material in this chapter.

Sanachem, one of the Sentrachem subsidiaries, has production sites in KwaZulu-Natal, Gauteng and Cape Provinces. Sanachem is an agrochemical company producing insecticides and pesticides. The KwaZulu-Natal site is situated at Canelands which is about 30 km north of Durban.

This company used water in the production of methyl isocyanate (MIC), pyrethroids, monosodium methylarsonate (MSMA), alachlor and bromoxynil octanoate processes. This water is used either as a solvent or for product washes. A substantial amount of water is also used in cooling towers (88 tons per day) and boiler make-up (45 tons per day). This water is discharged as effluent into the nearby river, the marine outfall and dedicated landfill sites. Other than the costs involved, i.e. R250.00 per kL, disposing of water via the marine outfall is still not much of a problem, since this effluent meets the existing regulatory criteria. However, landfill disposal continues to be one of Sanachem's main challenges as there is currently no landfill site for highly toxic waste in KwaZulu-Natal. This was accumulated and transported to Port Elizabeth at a cost of about R9 000/kL. The effluent treatment plant designed to remove arsenic in process streams, handled all the water flowing into the nearby river. The treatment process involved formed arsenic bearing solid waste which is classified as highly toxic waste. This too was transported across provincial borders to Port Elizabeth for disposal. According to Government policy, each province is responsible for its own waste, implying that toxic wastes from other provinces cannot be readily accepted in another province. The other solid waste, especially from the laboratories, is transported to the Shongweni landfill site.

In the face of these problems, Sanachem decided to invest in research for the development of a formal methodology to manage waste in a most sustainable manner. The applicability of water pinch analysis, as one of the emerging techniques for waste management and an integral part of cleaner production, was assessed. At the time of the study the available literature dealt mainly with continuous processes. However, most of the processes at Sanachem are batch, which called for the adaptation of the existing methodologies to batch processes. The processes were chosen on the basis of the nature of contaminants present in their effluent streams. It will be noticed that only those processes with the same major contaminant were used in the development of the methodology for batch processes.

5.1 OBJECTIVE OF STUDY

The study was aimed at assessing the applicability of WaterPinch principles in water demand reduction, waste minimisation and waste management in general, at Sanachem Canelands. This site contains a number of processes using water as a reaction solvent or a washing solvent for the final products. Consequently, water from these processes is contaminated with salts as well as traces of organic matter (pesticides) from the products. Due to the traces of pesticides, the hazard rating (HR) of most of these streams is quite high which implies that they can only be disposed of in high toxic waste sites, i.e. H:H sites. The streams with low toxicity are dispensed with via the sea outfall.

5.2 THEORY DEVELOPMENT

Batch processes, unlike continuous processes, are constrained with respect to time and concentration. Water reuse can only be effected subject to these two constraints. This implies that water can be used in another process if, and only if, it is available at the right time and concentration. Wang and Smith (1995b) have set the background for the application of water pinch analysis to batch processes. However, their approach assumed a semi-batch behaviour in processes, implying that water from one process could be reused in other processes even before the process is complete. This is related to the inclusion of water flow rates in their problem specification.

The application of the Wang and Smith technique to a sequence of actual batch processes at Sanachem, necessitated a number of modifications which were not immediately obvious. These modifications are outlined below:

1) The processes in question operate in a completely batch mode, which implies that a fixed amount of water is added to the vessel at the beginning of the water demanding process, and remains there until it is discharged at the end of the process. The semi-batch mode envisioned by Wang and Smith was then not applicable, since the reuse potential of water could only be realised after the completion, and not during the course of the process. Therefore, quantities rather than flow rates were relevant in the problem formulation.
2) It is evident that water flow rates appearing in the problem formulation (Wang and Smith, 1995) present themselves as equality constraints. However, a number of variations are possible in the way that the process constraints on quantity (or flow rate) present themselves. For instance, it could happen that there is no direct specification of the water quantity (or flow) in a particular stream, as long as the contaminant load and the outlet concentration are observed. Furthermore, the vessel probably has minimum and maximum levels for effective operation. In that case the water quantity falls away as an equality constraint, to become an inequality constraint, thereby changing the nature of the optimisation problem. The problem can be further complicated by allowing flexibility in the sequencing of batches during problem formulation. This is possible if different sequences give similar near-optimal solutions.
3) Wang and Smith did not consider that the first sequence will be different from the subsequent sequences. This implies that the water demand for the first sequence will be different from the water demand for the cyclic operation. This issue is discussed in **Sections 5.2.1.2** and **5.2.1.3**.

Therefore, it is important to recognise that there are several different forms which process constraints can take, and to consider these carefully when formulating the problem specification for pinch analysis.

To demonstrate the applicability of the above-mentioned adaptations to completely batch operations, an hypothetical set of processes was formulated. This example was drawn from experience at Sanachem. Initially, time is treated as the primary constraint and concentration as the secondary constraint. Subsequently, the priority of constraints is reversed so as to demonstrate the effect of the targeting procedure on the final design. Attention is also drawn to the fact that first sequence and cyclic-state targeting are essential in completely batch operations. The methodology by Doyle and Smith is also applied to batch processes.

5.2.1 Time Pinch Analysis

To illustrate the application of this analysis to completely batch processes, a hypothetical example for the production of an agrochemical which contains three organic components identified as A, B and C, was considered (This example resembled a process at Sanachem, but was simplified in some respects). These components are produced in batch reactors. All three reactions form sodium chloride (NaCl) as a by-product which is later removed from the final product. The removal of this by-product is effected by the use of fresh water. It is worth mentioning that, although the aim of the washes is to remove NaCl, there will be traces of organics in water. In formulating the problem, however, it was assumed that the concentration of these organics is virtually nil.

In the case of A, the reaction takes place in an organic solvent which is highly immiscible with water, so that water is required solely for washing the salt. In the case of B and C, however, water is used as the reaction solvent, and a further quantity is used for washing the product. While investigating this secondary washing of B and C, it was found that the salt load removed from the product was essentially zero due to the fact that most of it is removed with the reaction solvent water. However, it was considered that the washing step should not be discarded, as it constituted a quality control precaution in case of unforeseen process problems. The timing of the reaction and washing sequences was considered to be fixed by product requirements, which implies that there was no freedom to change the sequence to optimise the use of water.

5.2.1.1 Problem Specification for Pinch Analysis

The vessels operate in completely batch mode, implying that masses of water, rather than flow rates, are the relevant quantities.

Setting the concentration limits presented some conceptual difficulties. The situation for component A was straightforward, as laboratory tests have shown that acceptable product quality can only be achieved if fresh water is used at the start of the wash. The reaction solvent water for B and C was also easily specified, since the only requirement is that the salt must not precipitate, which sets the salt concentration at just less than 35 % by mass at the end of the reaction. Precipitation of salt leads to the erosion of glass lining in the reactors. The quantity of the wash water for B and C was based on experience. It was found that using water below 400 L led to lower product yields. This could be due to inefficient mixing in the vessel. The quantity of water was then set at 400 L.

The input concentration (which is clearly the same as the output concentration) should be set as low as possible without increasing the overall water use. These have been replaced by the variable x in Table 5.1. Due to the fact that the lowest concentration for contaminated water in this example is 0.1 kg salt/kg water, x was eventually set to this value. This constituted a radical departure from the type of specification envisaged by Wang and Smith (1995b).

Since the sequence of batch operations is repeated during production, waste water from the previous cycle would normally be potentially available for reuse, if storage facilities are provided. However this is not the case in the first cycle, so the targeting procedure for this first cycle is different from subsequent cycles.

Table 5.1: *Illustrative Problem Specification*

Process	Time	$C_{in,max}$	$C_{out,max}$	Water	Salt load
	[h]	[kg salt/kg water]		[kg]	
A wash	0 to 3	0	0.1	1 000	100
B reaction	0 to 4	0.25	0.51	280	72.8
B wash	4 to.5	x	x	400	0
C reaction	2 to 6	0.25	0.51	280	72.8
C wash	6 to 7.5	x	x	400	0
Total				**2 360**	**245.6**

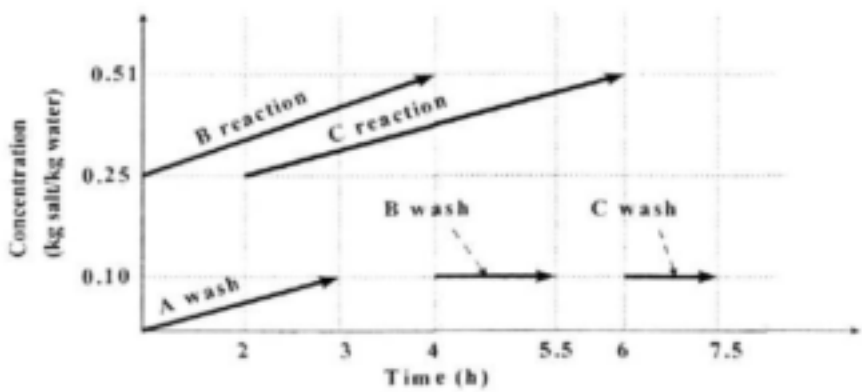


Figure 5.1: *Graphical representation of the problem specification, with x set to 0.1*

5.2.1.2 Targeting for the First Cycle

In Wang and Smith's method, the targeting procedure consists of dividing the problem into concentration intervals and time subintervals, with boundaries set by the endpoints of individual processes, and grouping together the streams that are required or available for reuse in each time subinterval. In each concentration interval, water which is available is reused, where possible, in its own time subinterval. Any surplus can be reused in subsequent time subintervals in the same concentration interval, or stored for reuse in later concentration intervals. Water cannot be reused in lower concentration intervals or in previous times. Any shortfall in any time subinterval can be made up from previous time subintervals, either from the same or lower concentration intervals. Fresh water is then used once all these opportunities have been exhausted. The eventual surplus becomes the system effluent, and the accumulated fresh water make up constitutes the system intake. According to this procedure, the capacity of storage that must be provided to achieve the minimum target can be identified. It will be realised during the analysis that this storage can be traded off against water use and effluent production.

This problem solution is such that in each time subinterval, the concentration constraint is met. This implies that, as long as water is available at the right time, it can safely be reused in any of the time subintervals within the concentration interval, i.e. the secondary constraint (concentration) is met in every step of the analysis, and the primary constraint (time) guides the formulation of the final solution (target design network).

To accommodate completely batch operations, the procedure is easily modified by recognising that water is required or available in discrete amounts, only at the beginning and end of both concentration and time intervals. The unknown concentrations (x) in the problem specification can be handled by repeating the calculations for a series of successively lower values for x, and selecting the lowest value that does not cause the overall water demand to increase.

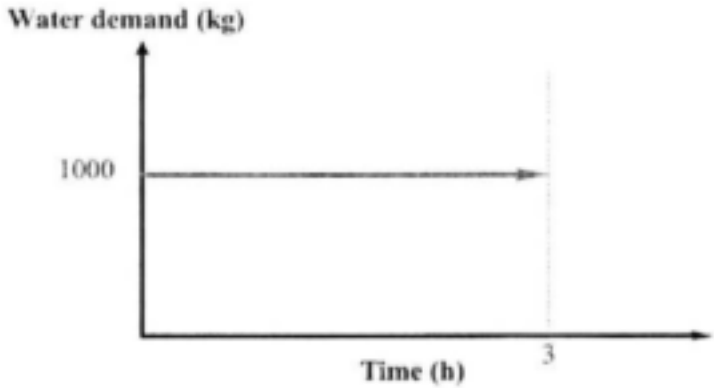


Figure 5.2: *Targeting interval (0 to 0.1) kg salt/kg water.*

Figures 5.2 to 5.4, show the targeting procedure with x set at 0.1 kg salt/kg water. Figure 5.4 shows targeting in the first concentration interval. Only process A is available in this interval, (see Figure 5.1), hence 1 000 kg of fresh water is required. Figure 5.2 depicts targeting in the concentration boundary. Both the washes lie in this boundary, since no load is removed from the product, and the concentration of water remains constant. Since each of the washes has a water demand of 400 kg, the overall water demand at the boundary is 800 kg as shown Figure 5.3.

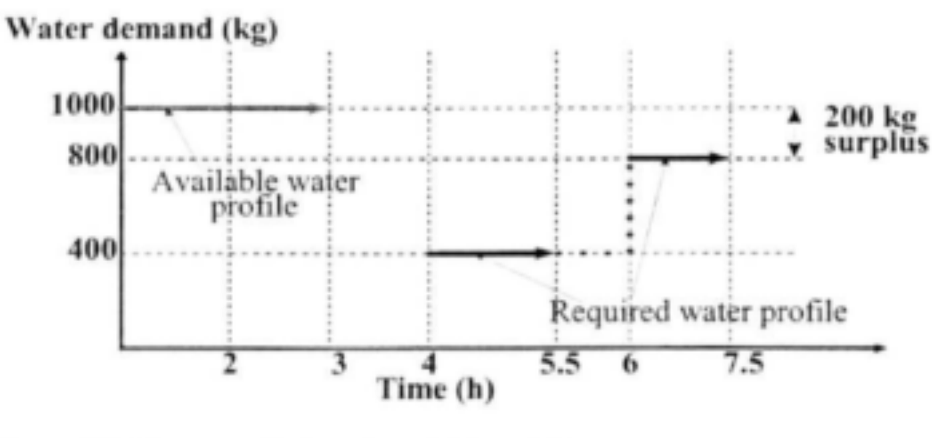


Figure 5.3: *Targeting the boundary 0.1 kg salt/kg water.*

Both B and C washes start after the completion of A wash. Moreover, the outlet concentration from the A wash corresponds to the required boundary concentration, i.e. 0.1 kg salt/kg water. Therefore, water from the A wash can be reused in B and C washes, with a surplus of 200 kg. However, this water cannot be used directly since A wash finishes

1 h before the start of B wash, and C wash only starts 3 h after the A wash. The time gap between the end of the A wash and the start of the B wash requires a storage facility with a capacity of 1 000 kg of water.

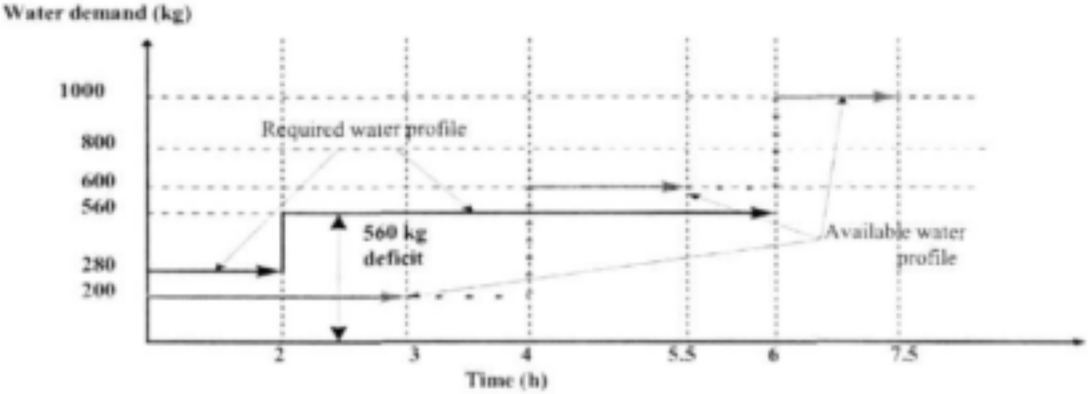


Figure 5.4: *Targeting interval (0.25 to 0.51) kg salt/kg water.*

Figure 5.4 represents targeting in interval (0.25 to 0.51) kg salt/kg water. This interval, as shown in Figure 5.1, has the B and the C reactions with an overall water demand of 560 kg. Since both these reactions start before the completion of the washing process of component A, no reusable water is available in the reaction time subintervals. This implies that fresh water will have to be used. The accumulated fresh water demand is, therefore, 1 560 kg. As this is the last concentration interval, this quantity is the target for the optimal design.

It is worth noting that interval (0.1 to 0.25) kg salt/kg water did not need to be considered since no processes fall within it: see Figure 5.1.

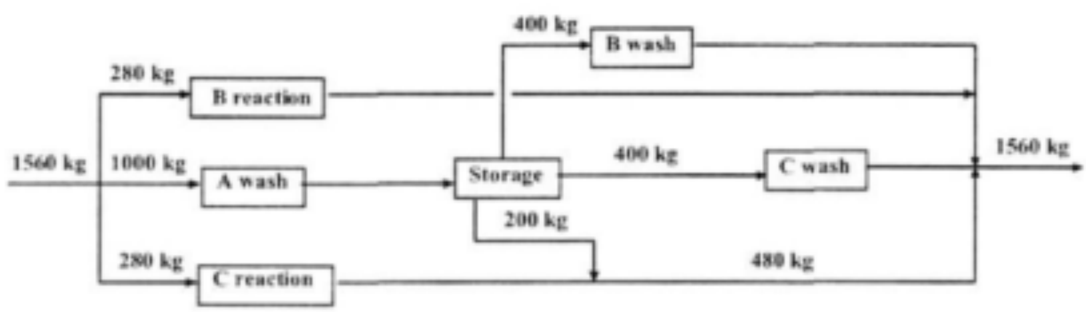


Figure 5.5: *Water reuse network resulting from pinch analysis (first cycle).*

It is typical of such problems that the solution shown in Figure 5.5 is not the only one that meets the minimum water use target.

5.2.1.3 Targetting for Subsequent Cycles

It is assumed that the process sequence in subsequent cycles is the same as the first cycle (although it is possible that would not be so). In this case, the time constraints simply fall away, as long as storage is available. Figure 5.6 shows one of the possible minimum water use configurations for the problem.

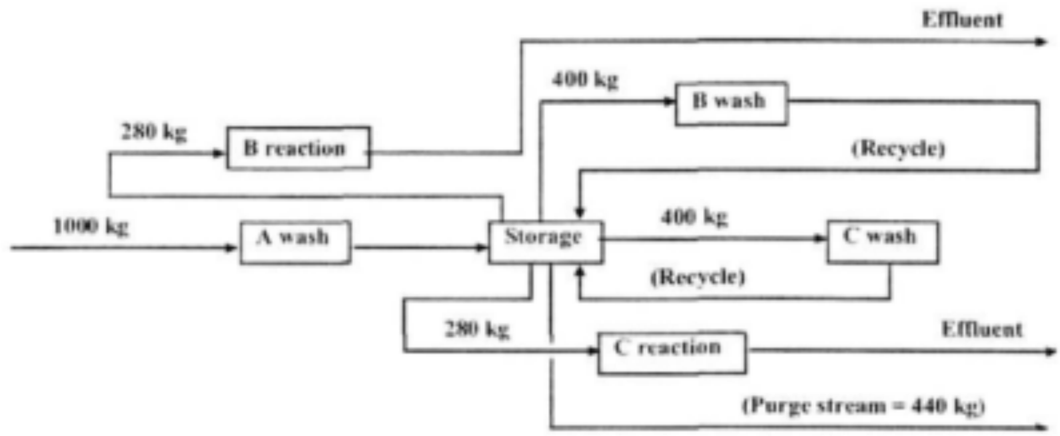


Figure 5.6: *Water reuse network resulting from pinch analysis (subsequent cycles).*

5.2.1.4 Storage

In general, there is a trade off between the capital cost of providing storage for intermediate effluents which could be reused and the running cost of extra water usage. However, the intrinsic storage potential of the process vessels themselves during their idle time should be considered in the analysis. Figure 5.7 indicates the storage potential for the illustrative problem.

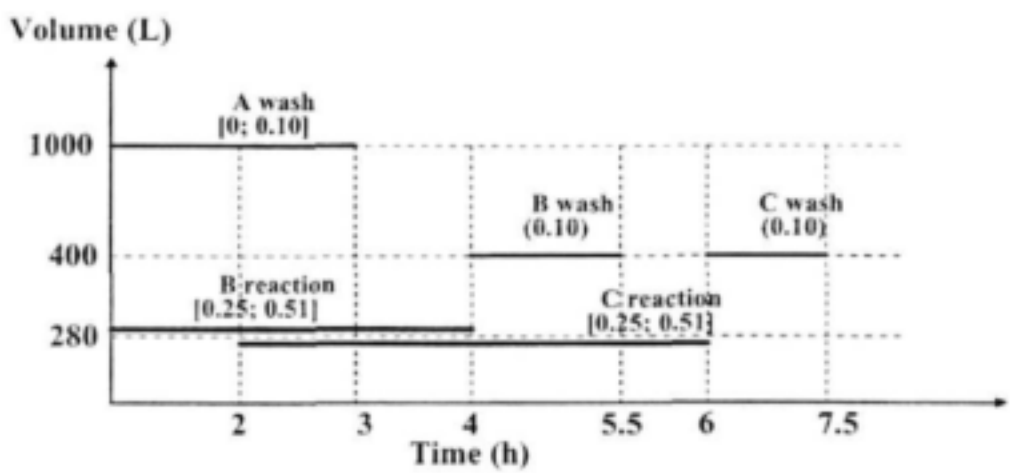


Figure 5.7: *Inherent storage availability diagram.*

It can be seen that the B and C wash vessels can be used to store water from the A wash, as these washes start well after the A wash has been completed. Figures 5.8 and 5.9 shows the resultant water reuse networks without any dedicated storage facility.

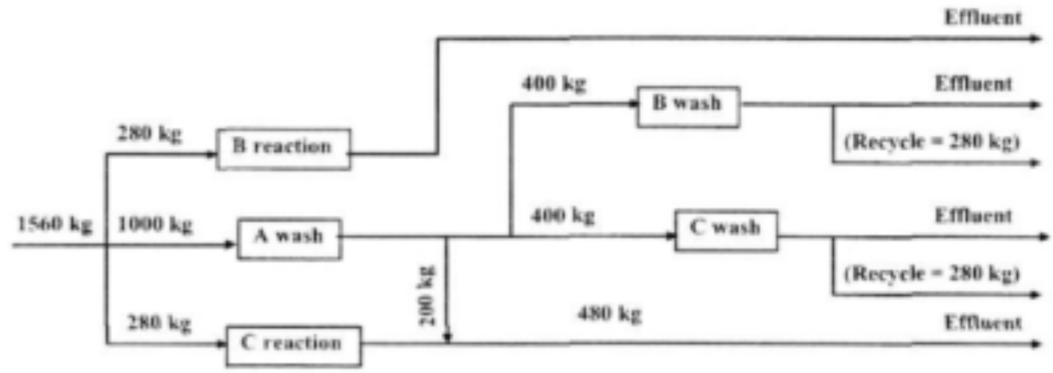


Figure 5.8: *Water reuse network with storage in process vessels (first cycle).*

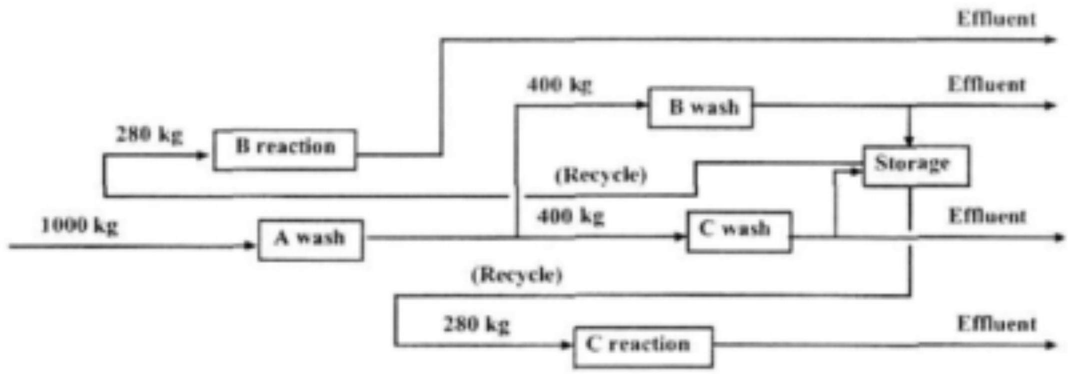


Figure 5.9: *Water reuse network with storage in process vessels (subsequent cycles).*

5.2.1.5 Mathematical Programming

The mathematical programming approach of Doyle and Smith (1997) is discussed in **Section 2.6**. Adapting it to the batch processes of the type described i the illustrative problem proved remarkably simple. A trivial step was to replace flow rates in the Doyle and Smith formulation with batch volumes (or masses). Time constraints were introduced by simply setting to zero any transfers which would require going backwards in time, or unavailable storage. The method yielded identical results to the manual methods described above. The major advantage of of the mathematical programming approach is that it readily deals with multiple contaminants, which are very awkward to handle with the manual targetting method.

5.3 Application at Sanachem, Canelands

A group of processes at the factory were selected for the case study, because they all involved the common "contaminant" NaCl, which is, in fact, reaction by-product in the formation of all the products involved. Bromoxynil octanoate is a herbicide, and fernvalerate and cypermethrin are pyrethrins (insecticides).

5.3.1 Process Descriptions

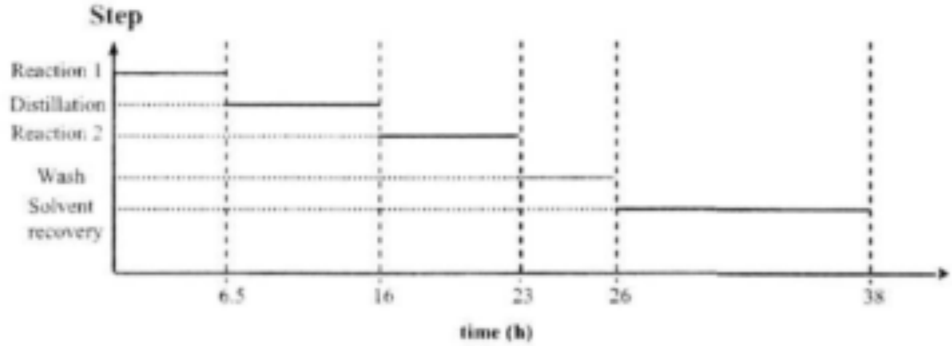


Figure 5.10: *Bromoxynil Octanoate production sequence.*

The process to produce bromoxynil octanoate involves two reaction steps. The first reaction forms the intermediate product bromoxynil with the evolution of water as a by-product, and takes an average of 6.5 h. Since the second reaction to form bromoxynil octanoate is adversely affected by the presence of water, the water from the first reaction is removed by vacuum distillation (-80 kPa) at about 80 °C. Some of the organic solvent is also carried over. The water-solvent vapor collects in the receiver as a binary phase mixture via the condenser. Water is then separated and put in a dedicated container. This step takes about 9.5 h and about 400 kg of water is removed. This water is later used in the washing step. Since the washing step requires 1 000 kg of water, 600 kg of fresh water is added. This explains the origin of this figure in Table 5.2. After water removal, the batch is drawn into the next reactor under vacuum where the second reaction takes place. This reaction takes about 7 h, after which water is introduced for washing the product of all impurities. NaCl is the main impurity, formed as a byproduct in the second reaction. The washing step takes 3 h. The last step in the entire process is solvent recovery, which takes about 12 h. This step takes place in a dedicated vessel and is effected by applying vacuum (-80 kPa) and raising the temperature to about 130 °C.

The pyrethroids cypermethrin and fernvalerate are produced by very similar processes, with exactly the same process steps, but different raw materials, and in different vessels. Figure 5.11 shows the sequence which applies to both products.

Figure 5.11: *Cypermethrin or Fernvalerate production sequence.*

The first step in the production of cypermethrin and fernvalerate is the reaction which takes about 7 h, assuming that all the potential process problems have been taken into account. These process problems are poor quality raw materials which tend to slow down the rate of reaction and the slow titration of one of the raw materials into the reactor. The reaction step uses 280 kg of water to dissolve one of the raw materials used in the process. After reaction, the batch is drawn under vacuum into the next vessel wherein the product wash is conducted to remove NaCl formed by the reaction. This takes about 1.5 h and uses 400 kg of water. This step is followed by solvent recovery in the same vessel. Solvent recovery takes an average of 4 h. It can be seen that three batches of cypermethrin/fernvalerate can be produced for every batch of bromoxynil ocatanoate.

5.3.2 Concentration limits

For bromoxynil octanoate, about 100 kg of salt (NaCl) is formed as a byproduct per batch. Since 1 000 kg of water is used, and only fresh water can be utilized, the maximum outlet concentration is 0.10 kg salt/kg water.

For cypermethrin and fernvalerate, it was discovered using the potentiometric method of analysis that almost all the salt is removed with the solvent water used in the reaction step. Since the solubility of salt under the reactor conditions is 35 % (m/m), and the reactor is lined with glass, the maximum outlet concentration was set at 34 % (m/m) in order to ensure that all the salt remains in solution so as to avoid the erosion of glass. This concentration corresponds to 0.51 kg salt/kg water. About 72.8 kg of salt is formed during reaction, therefore, the maximum inlet concentration was set at 0.25 kg salt/kg water.

Table 5.2: *Limiting process data for first production cycle*

Process	Time [h]	C_{in} [kg salt/kg water]	C_{out} [kg salt/kg water]	Water [kg]	Salt [kg]
Cypermethrin Reaction (1)	0 to7	0.25	0.51	280	72.8
Cypermethrin Wash (1)	7 to 8.5	0.10	0.10	400	0.0
Fernvalerate Reaction (1)	0 to7	0.25	0.51	280	72.8
Fernvalerate Wash (1)	7 to 8.5	0.10	0.10	400	0.0
Cypermethrin Reaction (2)	7 to 14	0.25	0.51	280	72.8
Cypermethrin Wash (2)	14 to 15.5	0.10	0.10	400	0.0
Fernvalerate Reaction (2)	7 to 14	0.25	0.51	280	72.8
Fernvalerate Wash (2)	14 to 15.5	0.10	0.10	400	0.0
Cypermethrin Reaction (3)	14 to 21	0.25	0.51	280	72.8
Cypermethrin **Wash (3)**	21 to 22.5	0.10	0.10	400	0.0
Fernvalerate Reaction (3)	14 to 21	0.25	0.51	280	72.8
Fernvalerate Wash (3)	21 to 22.5	0.10	0.10	400	0.0
B Octanoate Wash	23 to 26	0.00	0.10	600	60.0
Total				**4680**	**496.8**

As almost all of the salt is removed with the solvent water, very little, if any, salt is removed during the product washes. Also, the analysis conducted on the wash water did not measure a significant level of salt. However, it was decided to retain this step as a precautionary measure in case of process deviations. Since this step is used as a precaution, relatively clean water should be used so as to avoid product contamination. In this case study, other than fresh water, 0.10 kg salt/kg water is the least contamination level. This was then chosen as the concentration specification for the wash water. Since no load is removed, the inlet and the outlet concentrations in this step are the same. Table 5.2 summarises the discussion given in the foregoing paragraphs.

5.3.3 Results

The targeting calculations were carried out according to the procedures explained in **Section 5.2**. Accordingly, reuse configurations are shown for the first production cycle and subsequent cycles.

5.3.3.1 First Cycle

The final network based on this targeting procedure appears in Figure 5.12. In this diagram, C, F and B stand for cypermethrin, fernvalerate and bromoxynil octanoate, respectively. The subscripts r and w stand for reaction and wash, respectively. The existence of time gaps between washes requires the provision of storage. The diagram shows three storage blocks, however only one physical tank is actually required, because the three storage requirements occur at different times in the cycle It is clear in the diagram that water from the first wash is reused in the second and third washes for cypermethrin and fernvalerate. This water is later used in the bromoxynil octanoate wash prior to its disposal as effluent. All the water from the reactions is discharged as effluent, since it does not have any reuse potential.

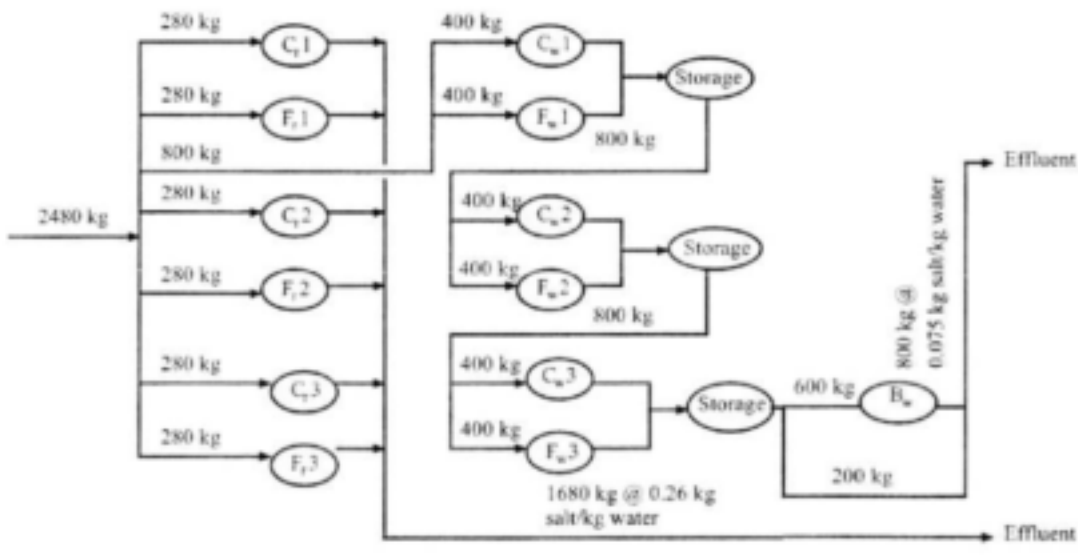


***Figure 5.12:** Reuse network for first production cycle.*

5.3.3.2 Subsequent cycles

The first cycle of production of bromoxynil octanoate takes 38 h, however the second cycle does not have to wait for the first to finish, because the second reaction and product washes take place in different vessels from the first reaction. Hence the each subsequent cycle can begin 16 hours after the previous one, as illustrated in Figure 5.13.

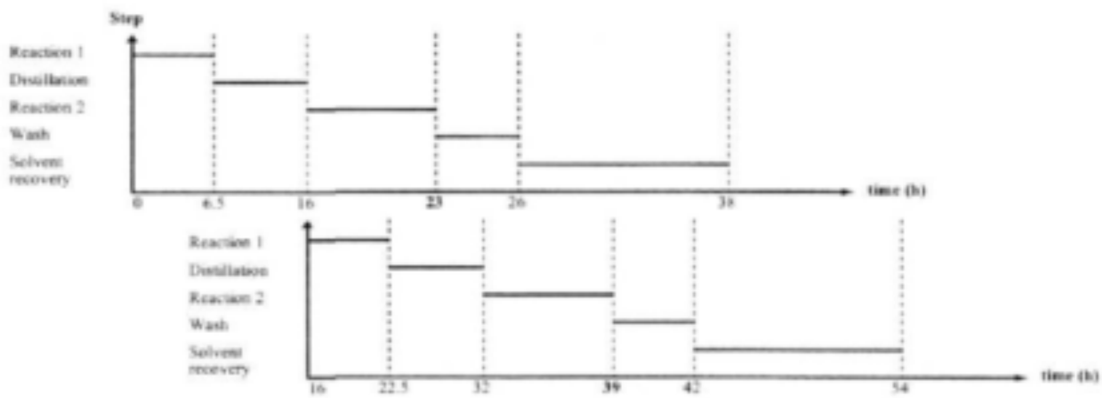


***Figure 5.13:** Overlapping bromoxynil octanoate production cycles.*

The combined schedule for the three processes under these conditions is shown in Table 5.3. The effect is that only two cypermethrin/fernvalerate batches can be produced per batch of bromoxynil octanoate.

***Table 5.3:** Limiting process data for subsequent production cycles*

Process	Time [h]	C_{in} [kg salt/kg water]	C_{out} [kg salt/kg water]	Water [kg]	Salt [kg]
Cypermethrin Reaction (1)	0 to7	0.25	0.51	280	72.8
Cypermethrin Wash (1)	7 to 8.5	0.10	0.10	400	0.0
Fernvalerate Reaction (1)	0 to7	0.25	0.51	280	72.8
Fernvalerate Wash (1)	7 to 8.5	0.10	0.10	400	0.0
Cypermethrin Reaction (2)	7 to 14	0.25	0.51	280	72.8
Cypermethrin Wash (2)	14 to 15.5	0.10	0.10	400	0.0
Fernvalerate Reaction (2)	7 to 14	0.25	0.51	280	72.8
Fernvalerate Wash (2)	14 to 15.5	0.10	0.10	400	0.0
B Octanoate Wash	16 to 19	0.00	0.10	600	60.0
Total				**3 320**	**351.2**

The corresponding reuse network appears in Figure 5.14

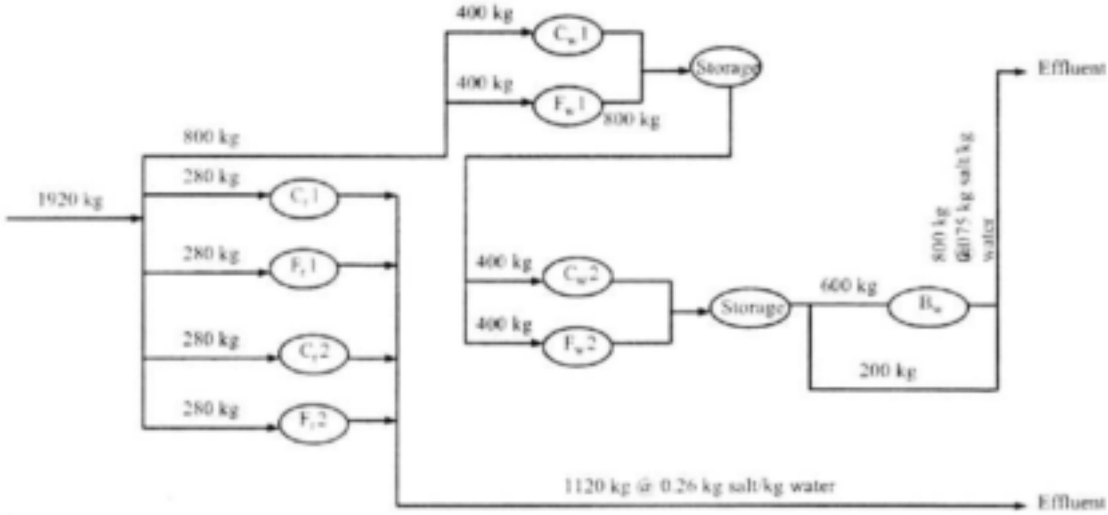


Figure 5.14: *Reuse network for subsequent production cycles.*

5.4 Conclusions

During the course of these investigations, an overall reduction of 96 kL per month of toxic effluent, 216 kL of non-toxic effluent, and an increase of 25 % in production capacity (due to reduced batch times) were identified as a result of the pinch analysis, together with other waste minimisation measures. This represented about a 40 % reduction in water use by the processes involved. Unfortunately, before the implementation stage was reached, Sanachem was bought by Dow Chemicals, and the processes in question were closed down as part of an international rationalisation program.

Although pinch analysis of batch processes have received little attention in the literature, this study showed that the methods developed for continuous processes can be adapted fairly readily. The main advantage of batch over continuous processes is their greater flexibility. In the pinch analysis context this means that the kinds of process constraints that have to be considered are more varied. This was demonstrated by the issue of the *fully batch* processes of this study, as opposed to the *semi-batch* processes considered by Wang and Smith (1995b). In practice, however, the basic ideas expressed in the literature need to be carefully adapted and extended to suit the nature of particular systems. The possibilities explored so far are by no means exhaustive, and a general method still has to be established. In drawing up such a general method, the effect of the different types of process constraints that may be encountered, and how these affect the targeting and network design methods, will have to be carefully considered. It is clear that, even in the same problem, different streams might be subject to different types of constraints. The mathematical programming approach of Doyle and Smith (1997) appears to offer the flexibility to address many of these issues.

6 THE LETHABO POWER STATION

A coal-fired power station contains a number of interconnected water-using systems, which present a number of opportunities to use membrane separation to recover water of suitable quality for reuse. The chief of these are: the condenser cooling circuit, the ultra-pure steam circuit, the potable water system for personnel as well as general factory use, and the ash-handling system. In addition, associated mining operations involve substantial flows of water, often contaminated, which may constitute both an opportune source of water if treated, and an environmental liability otherwise. Membrane applications which might be considered are: reverse osmosis (RO) or electrodialysis reversal (EDR) to concentrate the cooling water blowdown and return permeate to the cooling circuit; RO or nanofiltration (NF) pre-treatment of the feed to the ion exchange plant which produces ultrapure water for the steam circuit; NF treatment of mine water to upgrade it to a suitable quality for use in the power station systems; or ultrafiltration (UF) to provide potable water.

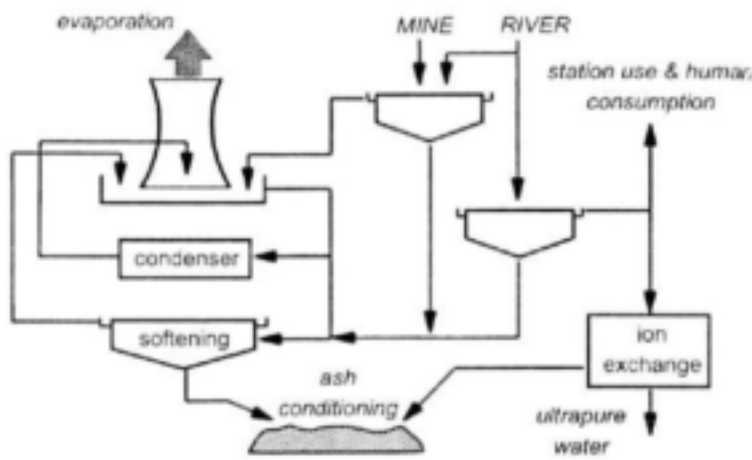


Figure 6.1: *Schematic diagram of water circuits at a coal-fired power station*

South Africa has a number of very large coal-fired power stations, concentrated in the coal fields of the province of Mpumalanga. This area also shares its relatively scarce water resources with the main mining and industrial region of the country, and indeed the availability of water is considered to be one of the chief limitations for economic development in the region. Consequently, it is a major concern of the national power utility, Eskom, to achieve the best possible water efficiency and the least possible environmental impact in operating their stations. Membrane processes have been an accepted part of Eskom's strategy for over a decade, with a large RO plant and a large EDR plant (recently replaced by a RO plant) operating at two of the more recently built stations. The membrane plants at these power stations recover desalinated water from the cooling circuit blowdown and return it to the circuit. Operating experience has led to questions as to whether this is the most effective role for a membrane regeneration process in the overall system. Water pinch analysis provides a systematic approach to determining the most effective location for a regeneration process in the system as a whole.

In this investigation, a start was made with formulating an approach to applying the principles of water pinch analysis to the water systems of a power station, with the particular objective of establishing the best use of an existing RO plant in the system. The study was based on the Lethabo Power Station located close to the Vaal river near Vereeniging, South Africa. This 3.6 GW plant is built adjacent to the opencast coal mine which supplies its fuel. The main source of water for cooling and for boiler operation is the Vaal River. The station was designed according to a *zero-liquid-effluent* philosophy, in which effluents are concentrated to the point where the residual volume can be accommodated on the coal-ash heaps, where the liquid serves a dust-suppression function. A tubular reverse osmosis (TRO) plant is used to achieve the necessary concentration ratio at times when this cannot be accomplished by evaporation alone: this only occurs occasionally, so the TRO plant does not operate continuously. The associated coal mine is a source of contaminated mine water, most of which was discharged at the time under a permit granted by the Department of Water Affairs, which was to be withdrawn, because of the quite severe problem of salination of the Vaal River.

The standard situation addressed by a pinch analysis calls for minimisation of the total amount of fresh water supplied to the set of processes. The situation under consideration here is more complex, because there is more than one water source (river water and mine water) and because increasing the salt concentration in the feed to the ion exchange increases the use of chemicals for regeneration. Furthermore, the use of mine water in the cooling circuit reduces the evaporation ratio that can be achieved, which ultimately increases the overall effluent discharged from the station, to the point where it can no longer be retained by the ash heaps. This appears to be precluded by Eskom's zero effluent discharge policy, but only if the power station is viewed in isolation from the mine. If they are considered together, it is clear that any mine water that the power station does not accept must be treated separately, or discharged to the environment.

Thus there is a balance that must be struck between use of river water, use of mine water, use of regeneration chemicals, and volume of effluents. This is represented in the model as a cost coefficient for each of these factors, which must have values which are in the correct relationship to one another. In principle, these should include a representation of relative environmental costs, not simply financial costs.

6.1 The Water Pinch Model of the Power Station

The water system was divided into five essential component sub-systems, as illustrated in Figure 6.2. This is a simplification of the actual system which omits a number of details.

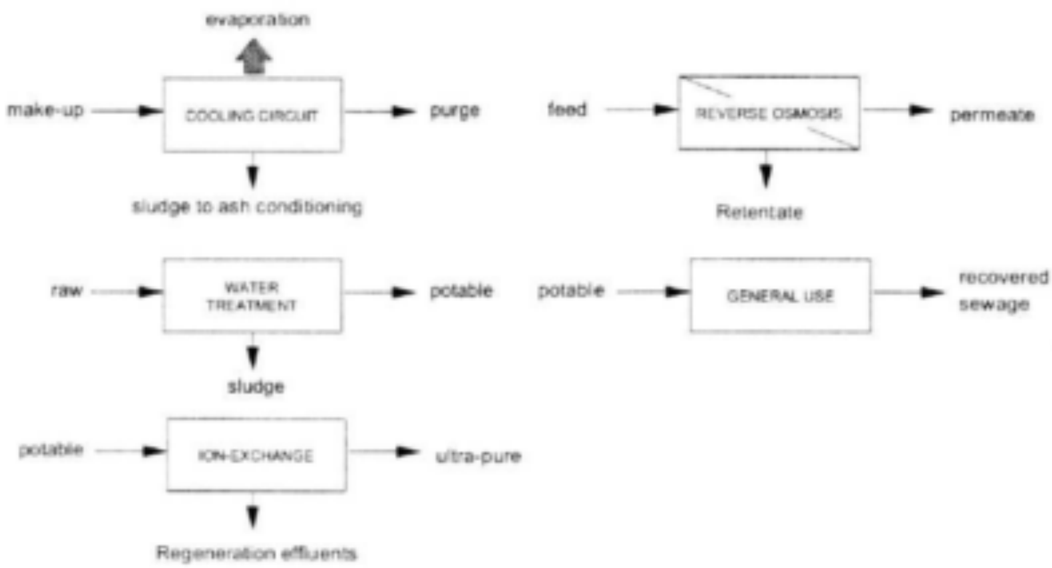


Figure 6.2: *The basic set of water circuit sub-systems used for the Pinch Analysis*

6.1.1 Modelling Simplifications and Assumptions

Because of the complexity of the optimisation procedures, it is desirable that the modelling of the individual processes should be as simple as possible, while still representing the essential behaviour of the system. The approach taken was to formulate material balances for the various units, with certain coefficients derived from plant records, which substitute for the equilibrium and kinetic relationships which would be required in a more fundamental model. Furthermore, since the optimisation is concerned with changing operating conditions, those parts of the system which may not be changed need not be modelled explicitly. Thus, for instance, the condenser circuit does not appear in the model, except indirectly in the cooling circuit model, in that it sets the evaporation rate and the limits on the concentrations.

Other notable omissions are the lime softeners and the potable water clarifiers. Here again, they are represented indirectly. The lime softening principally removes carbonate, which enters the system by atmospheric contact in the cooling towers, which constitutes an invariant load. The lime dosage to remove this carbonate is consequently also invariant, and the results are fixed concentrations of calcium and carbonate in the cooling circuit. Since there are no other significant sources of carbonate in the system, it was not considered as a variable contaminant, and the only way that this whole sub-system appears in the model is as a fixed calcium concentration in the cooling circuit model, which was presumed to be fixed by the solubility product of calcium carbonate (although the figure was obtained from the station records). In effect, this ignores the fact that the lime dosage would need to vary to maintain the fixed concentration as the flow network is modified; however it was assumed that the cost implications would be negligible.

Somewhat similar arguments were used for the suspended solids removed by the clarifiers, both in the cooling circuit and in potable water production. It was assumed that changes in the flow network would not significantly alter the flows of suspended solids or how they were removed, and there was consequently no need to include suspended solids in the model. The sludge flows indicated in figure 6.2 refer only to water and dissolved components. For these streams, the effect of solids was accounted for by flow rate constraints which prevented their being used for any purpose other than ash conditioning.

The storm water and station dam system was omitted for lack of flow rate and quality data at the time.

6.1.2 Conceptual structure of the model

The pinch analysis formalism allows (in principle) effluent from any sub-system to be recycled to the inlet of any sub-system (including itself). The matrix of these inter-system flows is taken as the set of variables in a constrained optimisation problem, with the constraints arising from process requirements with respect to the resulting concentrations and flowrates. In principle, all contaminants that can affect the various processed should be included in the model, together with the operational limits for the different processes. In practice, it is sometimes easier to use flow constraints to achieve the desired effect. A good example to illustrate this arises from the use of recovered sewage. Its use in potable water would be limited by the concentration of pathogenic micro-organisms, however the appropriate result is achieved by constraining the flow of recovered sewage to the potable water system to be zero, without including pathogens in the model as contaminants.

6.1.3 Mathematical Structure of the Model

Symbols:

- F_{ji} flow of (reused) water from outlet of process i to inlet of process j.
- F_{jk} flow of (fresh) water from source k to inlet of process j.
- c_{in} concentration of ion n in outlet stream from process i.
- c_{sn} concentration specification for ion n in the product stream from the ion-exchanger.
- δ_{in} mass gain of contaminant n over process i.
- W_i water gain over process i.
- z_n charge on ion n.

6.1.3.1 The Basic Model for Standard Processes

The standard model for a process node has a single input water stream and a single output. Mass transfers to non-aqueous streams are accounted for by specified gains in mass-flow of contaminant and/or water across the process (losses are represented as negative gains). These gains or losses are assumed to be independent of the flow or composition of the inlet water stream. The components of the power station model represented in this way were: the cooling circuit, production of sludge from the cooling circuit, potable water, potable water sludge, and the sewage recovery.

Balance for component n over process j.

$$\sum_i F_{ji}\, c_{in} + \sum_k F_{jk}\, c_{kn} + \delta_{jn} = \left(\sum_i F_{ji} + \sum_k F_{jk} + W_j\right) c_{jn} \qquad [6.1]$$

This is re-arranged as follows in order to solve for concentrations:

$$\left(\sum_i F_{ji} + \sum_k F_{jk} + W_j\right) c_{jn} - \sum_i F_{ji}\, c_{in} = \sum_k F_{jk}\, c_{kn} + \delta_{jn} \qquad [6.2]$$

The maximum water that can be reused from the process is limited to the outlet flow, which leads to:

$$\sum_i F_{ij} - \left(\sum_i F_{ji} + \sum_k F_{jk} + W_j\right) < 0 \qquad [6.3]$$

For a system where all the processes can be represented in this way, the set of equations [6.2] can be solved simultaneously for the concentrations if the values of all the flowrates are specified. A simple modification occurs where an outlet concentration is fixed at a known value, the equation for c_{jn} is replaced in the set by:

$$c_{jn} = X_{jn} \qquad [6.4]$$

where X_{jn} is the known fixed value. This situation occurs in the case of the calcium concentration in the cooling circuit, which is fixed by the solubility of calcium carbonate, since carbonate is continuously introduced by absorbtion of atmospheric carbon dioxide in the cooling towers.

This basic model was unable to represent the essential features of the ion exchange and RO processes, and special models had to be constructed.

6.1.3.2 A Simple Ion-Exchange Model.

The load of ion n removed from the feed water by the ion-exchanger is

$$L = \sum_i F_{ji} (c_{in} - c_{jn}) + \sum_k F_{jk}(c_{kn} - c_{jn}) \qquad [6.5]$$

The quantity of regenerant chemicals used is determined by the total number of equivalents removed from the product water, calculated as:

$$E = \sum_i F_{ji} (c_{in} - c_{jn})|z_n| + \sum_k F_{jk}(c_{kn} - c_{jn})|z_n| \qquad [6.6]$$

The quantities involved in making up regenerant solution are assumed to be proportional to E.

$$\text{Acid added} = A \times E \qquad [6.7]$$
$$\text{Base added} = B \times E \qquad [6.8]$$
$$\text{Dilution water added} = W \times E \qquad [6.9]$$

A, B and W are constants inferred from plant operating data.

The regenerant effluent stream was constructed by combining all the ions removed from the product water (L) with those added via the acid ($A \times E$) and the base ($B \times E$) in the dilution water ($W \times E$). This requires the ionic make-up of the acid and base used. Since the water used for dilution is ultrapure, taken from the ion-exchange product stream, the flow rate specification for the unit must be expressed as:

$$FlowSpec = \sum_i F_{ji} + \sum_k F_{jk} - W \times E \qquad [6.10]$$

6.1.3.3 A Simple Reverse Osmosis Model.

The RO plant has an overall water recovery R ($0<R<1$) and a permeate selectivity factor S_n for each solute n.

$$\left(\sum_i F_{mi} + \sum_k F_{mk}\right) c_{mn} - \sum_i F_{mi}\, c_{in} = \sum_k F_{mk}\, c_{kn} \qquad [6.11]$$

Here the subscript m represents the feed stream to the plant. If p represents the permeate, and r the retentate:

$$F_p = R \cdot \left(\sum_i F_{mi} + \sum_k F_{mk}\right) \qquad [6.12]$$
$$F_r = (1 - R) \cdot \left(\sum_i F_{mi} + \sum_k F_{mk}\right) \qquad [6.13]$$
$$c_{pn} = S_n \cdot c_{mn} \qquad [6.14]$$
$$c_{rn} = \left(\frac{1 - RS_n}{1 - S_n}\right) c_{mn} \qquad [6.15]$$

The component balance across process j becomes:

$$\left(\sum_i F_{ji} + \sum_k F_{jk} + W_j\right) c_{jn} - \sum_{i \neq m} F_{ji}\, c_{in} - \left[F_{jp} S_n + F_{jr}\left(\frac{1 - RS_n}{1 - S_n}\right)\right] c_{mn} = \sum_k F_{jk}\, c_{kn} + \delta_{jn} \qquad [6.16]$$

Across the membrane plant itself (process m) :

$$\left(\sum_i F_{mi} + \sum_k F_{mk} + W_m\right) c_{mn} - \left[F_{mp}S_n + F_{mm}\left(\frac{1 - RS_n}{1 - S_n}\right)\right] c_{mn} = \sum_k F_{mk}\, c_{kn} + \delta_{mn} \quad [6.17]$$

However, F_{mp} , W_m and δ_{mn} will all be zero except in very unusual cases.

The flow constraints for the membrane plant are:

Permeate: $$\sum_j F_{pj} - R \cdot (\sum_i F_{mi} + \sum_k F_{mk} + W_m) < 0 \quad [6.18]$$

Retentate: $$\sum_j F_{rj} - (1 - R) \cdot (\sum_i F_{mi} + \sum_k F_{mk} + W_m) < 0 \quad [6.19]$$

A further special constraint applies to the RO plant. The concentrations of calcium and sulphate in the retentate have to be limited to avoid scaling of the membranes due to precipitation of calcium sulphate. The critical parameter is K_{sp}, the effective solubility product of $CaSO_4.2H_2O$. This is strictly a function of the ionic strength of the solution; for simplicity the ionic strength was taken as fixed at a typical value observed on the plant. The constraint was then taken to be of the form:

$$c_{rCa} \cdot c_{rSO4} - K_{sp} < 0 \quad [6.20]$$

The equations and inequalities [6.2 to 6.4, 6.4 to 6.10, 6.12 to 20] constitute the basic model. To these were added specific constraints which limit individual values of concentration or flow rate according to particular process requirements.

6.1.3.4 Concentration and Flow Rate Constraints

Average flow rates over July 1997 for the various streams were obtained from a water usage report for the Lethabo Power Station. Concentration limits for the different systems were obtained from Eskom operating standards. In this preliminary analysis, only four ionic contaminant species were considered: Na^+, Cl^-, Ca^{++} and $SO_4^=$, which is a further simplification of the real situation. The parameters for the ion-exchange model (A, B and W) and the RO model (R and values of S_n for each ion) were inferred from the July 1997 report, and thus also represent average values for the month. The tubular RO plant at Lethabo operates at 75 % water recovery, and has a relatively low salt reject of 80 %.

The source concentrations and process concentrations used in the model are shown in Tables 6.1 and 6.2.

Table 6.1: *Contaminant levels in water sources*

	River [mg/L]	Mine [mg/L]
Cl	8.0	33.0
SO_4	14.0	458.0
Na	12.3	159.0
Ca	39.6	268.0

Table 6.2: Contaminant limits for processes

	Cooling circuit [mg/L]	Ash [mg/L]	Potable [mg/L]	Sludge [mg/L]	Recovered Sewage [mg/L]	Ultra Pure Water [mg/L]	RO brine [mg/L]	RO Permeate [mg/L]
Cl	400.0	-	200.0	202.0	-	0.0	-	-
SO_4	1000.0	-	250.0	252.0	-	0.0	K_{sp}	-
Na	500.0	-	500.0	502.0	-	0.0	-	-
Ca	240.0	-	48.0	48.0	-	0.0	K_{sp}	-

In the case of the RO brine, K_{sp} indicates that the Ca and SO_4 concentrations are limited by the solubility product relationship. The value of the constant (1.92×10^6 [mg/L]^2) was inferred from measured concentrations, rather than using a literature value, to account for the effect of other solutes on the solubility.

The flows that were taken as fixed were (ML /month):

Evaporation rate: 2753,5	Potable water: 232,3	Potable water sludge: 2,3
Ultrapure water: 104,8	Recovered sewage: 47,9	Ash conditioning: 86,9
Mine water: 114,0		

6.1.3.5 Other Process Constraints

As mentioned in the conceptual description of the model, various constraints can be accounted for indirectly by simply forbidding certain flow connections. Thus, the suspended solids in the clarifier sludges prevent re-use of those streams, and pathogens or dissolved organics in the recovered sewage limit its re-use to cooling circuit make up. The flow connections that were allowed are summarised in Table 6.3

Table 6.3: Connectivity matrix (0 - connection disallowed, 1 - connection allowed)

From \ To	Cooling	Ash	Potable	Sludge	Rec Sewage	UPW	RO feed
Cooling	0	1	0	0	0	0	1
Ash	0	0	0	0	0	0	0
Potable	0	0	0	1	1	1	0
Sludge	1	0	0	0	0	0	0
Rec Sewage	1	0	0	0	0	0	0
UPW	0	0	0	0	0	0	0
RO brine	1	1	0	0	0	0	0
RO Permeate	1	0	1	0	0	1	0
River	1	1	1	0	0	0	1
Mine	1	1	1	0	0	0	1

6.1.3.6 Objective Function

The objective function to be minimised was a sum of terms, each involving a simple cost coefficient and a quantity, as show in Table 6.4.

Table 6.4: *Cost coefficients used in the model objective function (R= South African Rand, 1997 values)*

Quantity	Coefficient	Quantity	Coefficient
Raw water used (ML/month)	759 (R/ML)	Water treated by RO (ML/month)	1 550 (R/ML)
Volume discharged (ML/month)	45 (R/ML)	Mine water used (ML/month)	45 (R/ML)
Salt removed by IX (keq/month)	819 (R/keq)	Salt discharged (t/month)	1 520 (R/t)

The flow-related coefficients were estimates supplied by power station personnel (the figure of 45 R/ML is a pumping cost only, the mine water is essentially a free resource). The ion-exchange cost was derived from the water usage report for the July 1997. The 1 520 R/t for discharging salt to the river is based on a study of the economic impact of salination of the Vaal River (Urban-Econ, 2000), which gives estimates of the cost to the South African economy as a whole of a rise in the salinity in the Vaal. The use of the coefficient in this way is debatable, as, unlike all the other coefficients, it does not represent a direct cost to the power station. It can be viewed as an attempt to provide an alternative to the regulatory approach which effectively permits free discharge now (albeit strongly discouraging it), with the prospect of a total ban (infinite cost) in the imminent future.

6.2 Results

From the forgoing development, it is clear that, because of simplifications in the model and the possibly controversial basis for the objective function, the results that can be presented are only possible scenarios for further investigation. The scenarios presented below were selected after running a series of other cases, which are not presented in detail, but which yielded the following general conclusions:

- if the power station was considered in isolation from the mine, the RO plant was not required at all; indeed up to about 30 ML/month of mine water could be used without bringing the RO plant into play, and without discharging any effluent beyond the capacity of the ash heaps to absorb the entire flow. This corresponded quite well with operating experience on the power station, and indicated that the model was at least realistic.
- if the cost of discharging salt was ignored, the low cost of the mine water caused the full quantity available to be used in the cooling circuit, once again without the RO plant running, however 46 t/month of salt were discharged to the environment.

When all the cost coefficients presented in Table 6.4 were included, (i.e. including the environmental cost of discharging salt) the model used all the available mine water, and employed the RO plant to reduce the effluent volume to the ash capacity, resulting in no liquid discharge to the environment. The optimal arrangement of flows for this case is shown in Figure 6.3.

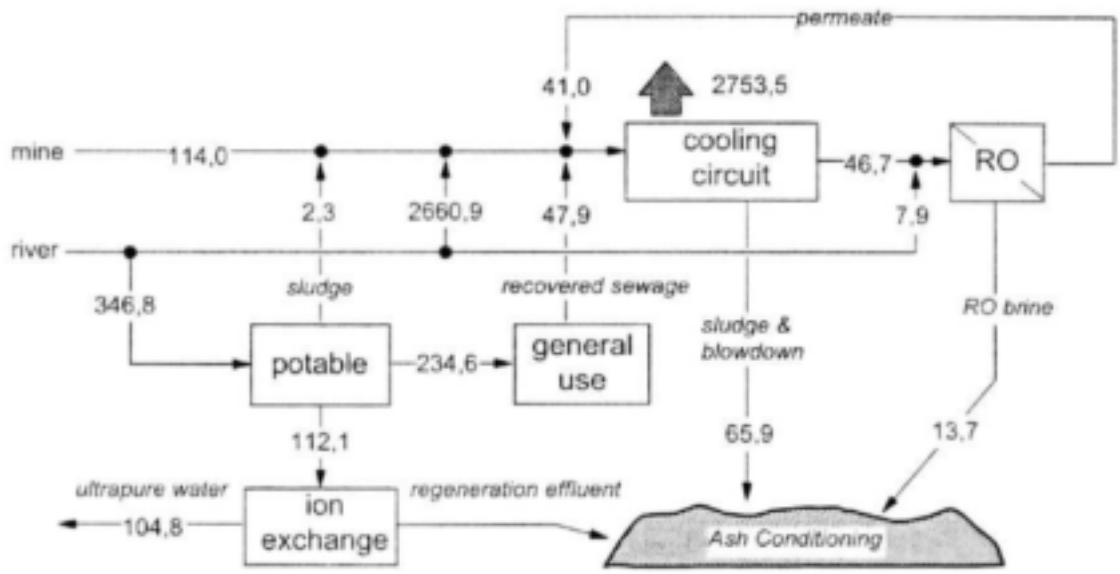


Figure 6.3: *Optimal configuration determined using the cost coefficients in Table 6.4 (flow rates in ML /month).*

The estimated R1 520 per tonne salination impact involves considerable uncertainty, so a sensitivity analysis was carried out. The threshold between the RO plant operating or not operating was found to be R1 150 per tonne, which allows for a reasonable margin of error in the coefficient.

Up to this point, only changes to the flow configuration using the existing equipment had been considered, that is, changes which require modification of the pipework only. The TRO plant at Lethabo was relatively inefficient and expensive to operate in comparison with more modern designs. Data from the recently installed spiral RO plant at the Tutuka power station was used to generate the scenario shown in Figure 6.4.

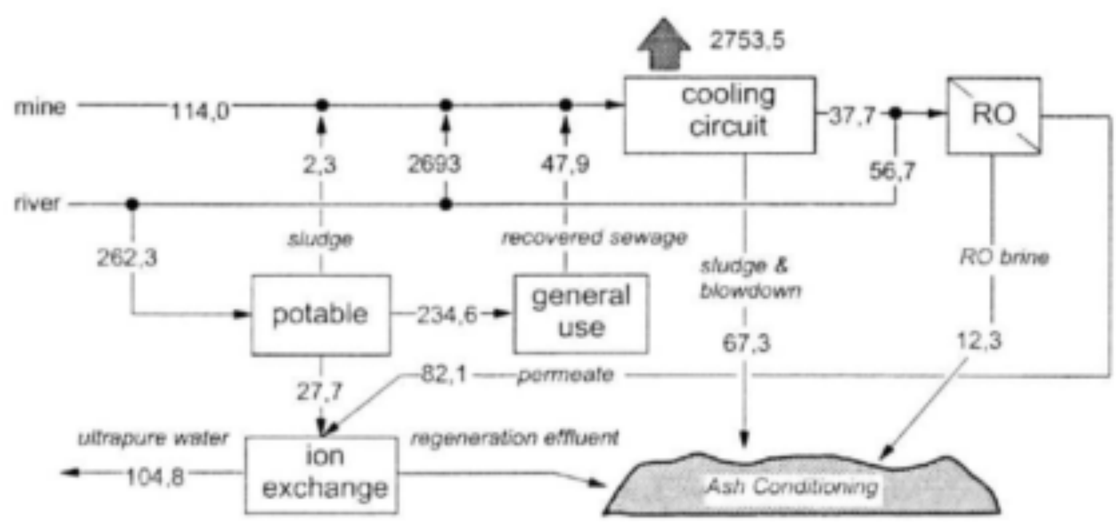


Figure 6.3: *Optimal flow rates for a high efficiency spiral RO plant (flow rates in ML /month).*

The parameters for the spiral RO plant were 97 % salt rejection, 87 % water recovery, and an operating cost of R900 per ML of feed, otherwise the cost coefficients were as before (Table 6.4). The most striking feature of this solution was that the primary role of the RO plant had changed from balancing the cooling circuit, in order to prevent discharge of salts to the environment, to pretreating the feed to the ion-exchange plant, in order reduce consumption of regenerant chemicals. This new configuration results in a saving of R16 700 per month over the previous one, which represents the incentive to invest capital in a new RO plant.

6.3 Conclusions

Although the model is not sufficiently complete for the results to be considered definitive, it appears to represent enough of the essential characteristics of the power station for the results to be realistic. The cases considered indicate that:

- It is technically feasibly to run the mine and the power station together on a zero-liquid-effluent basis, which captures all the saline effluents on the ash heaps, by using the existing TRO plant.
- An incentive is needed to justify this economically. It appears that the magnitude of this required incentive is of the order of the cost to the national economy of salination of the water supply, which should be of interest to regulatory authorities. Eskom is currently sponsoring research to develop a decision-support methodology which can take into account issues like this, which are difficult to quantify in purely techno-economic terms.
- The optimal role of a membrane plant changes as its technical performance characteristics and its operating cost change.

This case study was the first in which the reactivity of species in the water was taken into account. In terms of the distinction between utility and process water, referred to in **Section 3.3** on the scope of a pinch analysis, this system represents an in-between case - the role of water the power station is clearly that of a utility, yet the issues of reacting species were important in the analysis. This situation arose because of the extreme demands that the power station places on the water it uses, in terms of evaporation ratios for the cooling water and purity for the steam circuit, which make the extent of water treatment required to keep it fit for use a highly significant factor in the analysis.

If, at a simple level, one considers the power station in isolation, and looks only at the water use, the evaporation is the dominant flow, and the pinch analysis can only optimise the minor flows, which will not have a major effect on the overall water use. However, if one considers that the problem is not really with the water flows, but the salt flow, then the salt remains with the minor flows, and it becomes important to get them right. So it might be better to think in terms of a *salt pinch* rather than a *water pinch* problem. This becomes even more relevant if the mine is considered as part of the system.

7 OTHER INVESTIGATIONS

This chapter briefly describes those investigations which were not completed during the project period. Even though they did not reach satisfactory conclusions in themselves, they added to the experience of undertaking such investigations, and thereby contributed to the *Guide to Conduction a Water Pinch Analysis Investigation* presented in **Chapter 3**.

7.1 SA Tioxide

Tioxide Southern Africa (TSA), at that time a member of the Tioxide Group Ltd. world wide, is a producer of a white Titanium dioxide pigment, which is used, amongst others, in the paint, paper, food and cosmetics industries.

TSA produces this pigment by applying the Sulphate Process, which is a process whereby a raw 83% rich titanium dioxide ore is reacted with sulphuric acid to produce a titanium pulp. This pulp is then washed as the ore contains iron and other metals which are harmful to the crystal growth of titanium dioxide crystals. The washed pulp is then allowed to crystallise by calcination. The pigment is then milled to reduce the agglomerated crystals to single crystals in the size range of < 20 mm and packed into bags for selling. In the TSA sulphate process, 44 tonnes of water are used per tonne of pigment produced. This fresh water comes from the Umbogintwini River (treated by AECI Operational Services AOS) and from Umgeni Water, and liquid effluent leaves TSA at a rate of ca. 1600 Ml / annum (1996 figures) via the Tioxide pipeline into the Indian Ocean just off the coast of Southern Durban.

The investigation was started in 1997 by Paul Henry, who received excellent support from the factory. He spent several months in the Tioxide factory working almost as an operator to familiarise himself with the process, and compile a water balance. A preliminary pinch analysis was attempted, using iron as the critical contaminant, however this led to apparently contradictory results. It was suggested that these were probably due to the multiple contaminant nature of the problem. At the time we had not made much progress with techniques to deal with multiple contaminants, and it was recommended that this should be an important direction for further work.

At this point Mr. Henry left the University of Natal, and attempts to find a replacement investigator were unsuccessful. A seemingly ideal opportunity to use a former SA Tioxide employee to continue the research failed most unexpectedly at the last moment when it turned out that there had been an unresolved employment issue at the time he had resigned, and he was not accepted by the company.

It is probably, however, that we would have not been able to make much more progress at the time, as the theoretical basis for dealing with multiple contaminants, and with chemically reacting components had not been developed.

7.2 AECI Bioproducts

The AECI Bioproducts plant at Umbogintwini was one of the first to be selected for water pinch investigation at the start of the project in 1997, as it is one of the major users of freshwater on the complex and hence discharges a commensurate quantity of wastewater, amounting to approximately 400 ML per annum. Bioproducts is a manufacturer of l-lysine, which is an animal feed additive.

Commissioned in 1995, AECI Bioproducts is a modern facility and has sophisticated quality and environmental standards. Freshwater is withdrawn from the Umbogintwini River and is pre-treated before use. The l-lysine is produced by batch fermentation and is extracted from the fermentation broth by ion exchange. Two effluent sources arise from the manufacturing process: a concentrated broth effluent and general process effluent, which are handled separately. Process effluent arises mainly from the following sources:

- the utility system;
- tank and unit operation cleaning;
- pump seals;
- storm water runoff and
- contaminated process condensate.

Process effluent is discharged via a sea pipeline and stringent environmental regulations limited the concentration of pollutants expelled in this manner. What remains after lysine extraction is broth effluent, which is removed from the site and handled by a local sewage works. In accordance with an agreement with the Department of Water Affairs and Forestry (DWAF), neither broth effluent nor failed fermentation batches were to be discharged via the sea pipeline.

Umbogintwini Operating Services (UOS) is an effluent and water treatment facility that exists at the industrial complex. Umbogintwini river water is treated to an acceptable level of concentration by UOS for use in the plants at the complex. Some industries utilise the UOS effluent treatment facilities, however the Bioproducts process effluent is of a suitable quality for direct discharge via the sea pipeline; no additional treatment is required. Barring pH correction of the broth effluent, no onsite effluent treatment takes place. The degree of integration in the system is high; clean process condensate is reused in several operations.

The investigation by Grant Gardner began well. The factory designated a process engineer, Mike Greening, to provide internal support. A preliminary process flow sheet and water balance were drawn up. However, at this point Mike Greening left the company, and the investigation came to a halt; Grant Gardner turned his attention to the Sasol Polymers chlor-alkali plant..

In 1999, at the request of DWAF, the investigation was restarted by another MScEng student, Janos Schneider. By this time it had become feasible to undertake a multi-contaminant pinch analysis, which meant that the data gathering had to be re-visited. At the end of the project period the investigation was still in the data gathering stage, and was carried over to the follow up project K5/1158 *The Further Application and Development of Pinch Analysis for Water and Effluent.*

7.3 Mondi Merebank Paper Mill

This investigation was the first of what developed into a significant relationship with the paper industry, involving the two major groups Mondi and Sappi. It was started in 1999 through Gladys Naylor (née Crampton), a process engineer at Mondi Merebank. She registered for a part-time MScEng to undertake pinch analysis of parts of the Merebank paper mill.

Mondi Paper, a division of Mondi Ltd., produces pulp from softwood timber using groundwood and thermo-mechanical pulping and from recycled fibre (waste paper). The pulp is used, together with purchased chemical wood pulp, to produce approximately 500 000 t/y of various paper products. In addition some of the uncoated woodfree paper produced is used as base paper for producing approximately 12 000 t/y of carbonless coated paper.

The paper making process is a large user of water and the shortage of water resources in South Africa has made it imperative for industry to make the most effective use of water and recycle as much as possible for re-use within the process.

The incentives for process water recycling include:

- Improved economy
- Smaller volume of effluent per ton of paper produced
- Potential fibre savings

There are however, difficulties associated with recycling water, for example difficulties with wire and felt cleaning on the paper machine, formation of slime, objectionable odour and increased corrosion. Adverse effects are associated with the build-up of dissolved organic and inorganic substances. Their presence in the paper making system causes a higher cationic demand, thereby increasing the amount of cationic retention aid required to achieve optimum flocculation.

Water is used as transport and processing medium. Water is essential in developing hydrogen bonds between fibres which gives paper its strength. Water is also used as dilution water for chemicals, coolant in process equipment, sealant in vacuum pumps and as cleaning fluid of equipment surfaces. Fresh water is introduced to the process mainly through paper machine wire and press section showers and is then led counter-currently to various washing and diluting duties in the pulp production plant. The role of the showers is to lubricate and to keep the fabrics used to support the paper web clean. Shower water is heated (40 to 60 °C) in the paper machine heat recovery system.

Recycling of process water is restricted by water soluble materials released from fibre and other raw materials. Especially in mechanical pulping, lignin, carbohydrates, resin and fatty acids are dissolved or dispersed into process water.

The solubility of wood components depends on the quality of raw material, temperature, pH, residence time, turbulence of mixing and consistency. For example, at boiling water conditions the amount of material dissolved is three times the amount dissolved at room temperature, measured as COD.

The concentration of dissolved and colloidal substances in the short circulation (forming section - silo - deculator - headbox) depends on their retention on the paper and on the intake of fresh water. Introduction of fresh water to the short circulation of the paper machine will help the paper maker to keep the process clean.

The extent to which the different substances accumulate in circulation waters with increased recycling is not well known. Based on laboratory work, higher concentrations are known to impair paper quality and to increase biochemical activity in the process water. As a result harmful deposits may form and in anaerobic conditions unpleasant smell and acidic corrosive compounds are formed. It is estimated that the reduction of water consumption to one third would increase the COD value by a factor of four.

In addition to releases from fibre itself, a significant amount of dissolved solids originates from chemicals used in the process. Furthermore, harmful contaminants enter the water circulation through the broke system. These contaminants can be especially problematic when coated grades are produced.

At the end of the project period, this investigation was still in the data gathering phase, and it was carried over to the follow up WRC project K5/1158 *The Further Application and Development of Pinch Analysis for Water and Effluent*.

8 CONCLUSIONS AND RECOMMENDATIONS

This project represented a new field for the researchers involved, and the case studies that were undertaken met with a mixture of successes and failures, with some incomplete at the end of the project period. The *Guide to Conducting a Water Pinch Analysis Investigation* presented in Chapter 2 of the report attempts to summarise the experience gained during these investigations, and is perhaps the chief immediate outcome of the project.

Industrial awareness of the technique in South Africa has been raised through direct interaction with industries involved in the case studies and through conference papers, workshops and courses presented during the project, however there is a way to go before water pinch analysis can be considered as an accepted and establish practice.

8.1 Conclusions

The following general conclusions can be drawn about the significance of water pinch analysis:

1) A water pinch analysis provides a clear and systematic picture of the water requirements of a system of processes, subject to the constraints imposed by the technology of the processes and the environment in which they operate.
2) By identifying the factors which limit further reduction in the water requirements, the technique can focus attention on those areas of the process where technological improvements will be most beneficial in improving water efficiency.
3) By quantifying the impacts of technological and regulatory limits on a process, water pinch analysis has the potential to provide a rational tool for negotiation between an industry, water authorities and other role players.
4) Currently published water pinch theory is suited to analysing water which is used in a process as a utility; it is less suitable for situations where water is intrinsic to the technology of the process, for example in a hydrometallurgical process.
5) Because South Africa is a water-scarce country, many South African industries have responded to pressure to conserve water, and already have processes which use water relatively efficiently when compared to many industrialised countries. This means that dramatic savings in water use, as sometimes claimed in the international literature, are often not as readily available in South Africa.
6) There is a need for a scoping technique to provide a rapid assessment of a process to estimate the scope that it offers for improvement as a result of conducting a water pinch analysis.
7) Gathering the necessary data on a system is almost always the most difficult and most time-consuming step in a water pinch analysis. It is unlikely that all the required data will be obtained at the first attempt, and so an iterative process which alternates between data gathering and analysis occurs.
8) It is difficult, if not impossible, for an effective pinch investigation to be undertaken by a consultant outside the industrial organisation concerned, unless it is done with the full commitment and participation of the organisation at all stages.

8.2 Recommendations

1) Further efforts are required to encourage wider acceptance of water pinch analysis by South African industry. This should be undertaken in conjunction with industry on a case study basis.
2) Further work is needed to extend the water pinch analysis methodology to account for chemically reacting solutes and aqueous reagents.
3) Techniques for the early identification of the applicability of water pinch need to be developed.
4) Techniques need to be developed to reduce the time and effort required to gather the data needed for a water pinch analysis.
5) The use of water pinch analysis as a tool for co-regulation should be explored. This will require studies in which regulatory authorities are involved as partners, and the development of a a protocol for reporting the modelling assumptions and process limits used in an analysis in a transparent and auditable way, so that it can be used with confidence in negotiations between industrial and regulatory parties.
6) Local consultants should be encouraged to set up a water pinch analysis service to industry.
7) The energy efficiency of a process has a significant impact on its water use for cooling and the concomitant generation of saline effluents. The simultaneous optimisation of water and energy use is therefore an important direction for further investigation.

9 REFERENCES

Alva-Argaez, A., Kokossis, A. C., Smith, R. (1998) Process Integration for Wastewater Treatment Systems. *1998 AIChE Annual Meeting*. Miami Beach, Florida.

Buehner, F. W., Rossiter A. P. (1996). Minimize waste by process design. *Chem. Tech*, (April): 64 - 72.

Crabtree, E. W., El-Halwagi, M.M. (1995). Synthesis of environmentally-acceptable reactions. *AIChE Symposium Series*, **90**(303): 117-127.

Dantus, M.M., High, K. A., (1996) Economic Evaluation for the Retrofit of Chemical Processes through Waste Minimisation and Process Integration. *Ind. Eng. Chem. Res*, **35**: 4566-4578.

Dhole, V. R., Ramchandani, N., Tainsh, R.A., Wasilewski, M. (1996). Make your process water pay for itself. *Chemical Engineering* (January).

Doyle, S.J. and Smith, R. (1997). Targeting Water Reuse with Multiple Contaminants. *Trans IChemE*, **75**, Part B, 181-189.

Dunn, R.F., Zhu, M., Srinivas, B.K., El-Halwagi, M.M. (1995). Optimal design of energy-induced separation networks for VOC recovery. *AIChE Symposium Series*, **90**(303): 74-85.

Dye, S. R., Berry, D.A.,Ng, K.M. (1995). Synthesis of crystallization-based separation schemes. *AIChE Symposium Series*, **91**(304): 238-241.

El-Halwagi, M. M., Manousiouthakis, V. (1989). Synthesis of mass exchange networks. *AIChE Jl.*, **8**: 1233-1244.

El-Halwagi, M. M., Manousiouthakis, V. (1990a). Automatic synthesis of mass exchange networks with single component targets. *Chem Eng Sci.*, **9**: 2813-2831.

El-Halwagi, M. M., Manousiouthakis, V. (1990b). Simultaneous synthesis of mass exchange and regenerative networks. *AIChE Jl.*, **36**: 1209-1219.

El-Halwagi, M. M. (1992). Synthesis of reverse osmosis networks for waste reduction. *IChE Jl.*, **38**(8): 1185-1198.

El-Halwagi, M. M., Srinivas, B.K. (1992). Synthesis of reactive mass exchanger networks. *Chem. Eng. Sci.*, **47**(8): 2113-2119.

El-Halwagi, M. M., El-Halwagi, A. M., Manousiouthakis V. (1992). Optimal design of dephenolization networks for petroleum-refinery wastes. *Trans. IChemE* Part B, **70**: 131-139.

El-Halwagi, M.M. (1995). Introduction to Numerical Optimization Approaches to Pollution Prevention, in *Waste Minimisation Through Process Design*, A.P. Rossiter, Editor., McGraw-Hill: New York. p. 199-207.

El-Halwagi, M. M., Hamad A.A. (1996). Synthesis of waste interception networks and allocation networks. *AIChE Jl.*, **42**: 3087-3101.

El-Halwagi, M. M. (1997). *Pollution Prevention through Process Integration. Systematic Design Tools*, Academic Press, San Diego.

Gardner, G.A., (2000) Liquid Waste Minimisation on a Chloro-alkali Complex, *MScEng Thesis*, University of Natal.

Grossman, I.E., Caballero, J. A., Yeomans, H. (1999) Advances in Mathematical Programming for Automated Design, Integration and Operation of Chemical Processes. *PI '99*. Copenhagen, Denmark

Kemp, I.C. and Macdonald, E.K., (1987). *IChemE Symposium Series*, **105**, 185-200

Kemp, I.C. and Macdonald, E.K., (1988). *IChemE Symposium Series*, **109**, 239-257

Kemp, I.. C., and Deakin, A. W., (1989), The cascade analysis for energy and process integration of batch processes, Part 1, *Chem Eng Res Des*, **67**: 495 - 509.

Kemp, I. C., and Deakin, A. W., (1989), The cascade analysis for energy and process integration of batch processes, Part 2, *Chem Eng Res Des*, **67**: 510 - 516.

Kemp, I. C., and Deakin, A. W., (1989), The cascade analysis for energy and process integration of batch processes, Part 3, *Chem Eng Res Des*. **67**: 517 - 525.

Kiperstock, A., Sharratt, P.N. (1995). On the optimisation of mass exchange networks for the removal of pollutants. *Trans IChemE.*, **73**: 271-277.

Kuo, W.-C.J., Smith, R., (1997) Effluent Treatment System Design. *Chem. Eng Sci.*, **52**(23): 4273-4290.

Kuo, W.-C.J., Smith, R., (1998a) Designing for the Interaction Between Water-Use and Effluent Reduction. *Trans IChemE*, **76**, Part A : 287-301.

Koolen, J.L.A., de Wispelaere, G., Dauwe, R. (1999). Optimisation of an Integrated Chemical Complex and Evaluation of it's Vulnerability. *2nd Conference on Process Integration, Modeling and Optimisation for Energy Saving and Pollution Reduction*. Budapest, Hungary.

Kuo, W.-C.J., Smith. R., (1998b) Design of Water-Using Systems Involving Regeneration. *Trans IChemE*, **76**, Part B : 94-114.

Lakshmanan, A., Biegler, L.T (1995). Reactor network targeting for waste minimisation. *AIChE Symposium Series*, **90**(303): 98-104.

Linnhoff, B., Flower, J.R. (1978). Synthesis of heat exchanger networks, Part 1: Systematic generation of energy optimal networks. Part 2 : Evolutionary generation of networks with various criteria of optimality. *AIChE Jl.*, **24**(4): 633-654.

Linnhoff, B., Mason, D.R., Wardle, I. (1979). Understanding heat exchanger networks. *Comput. Chem. Eng.*, **3**, 295-302.

Linnhoff, B., Hindmarsh, E. (1983). The pinch design method of heat exchanger networks. *Chem Eng Sci*, **38**(5): 745-763.

Linnhoff, B., Townsend, D.W. (1983). Heat and power networks in process design. Part I: Criteria for the placement of heat engines and heat pumps in process networks. Part II: Design procedure for equipment selection and process matching. *AIChE Jl.*, **29**(5): 742-771.

Linnhoff, B., Townsend, D.W., Boland, D., Hewitt, G.F., Thomas, B.E.A., Guy, A.R., Marsland, R.H. (1994). *User Guide on process integration for the efficient use of energy* , IChemE., Rugby, U.K.

Linnhoff, B., Akinradewo, C. G., (1999) Linking Process Simulation and Process Integration. *Comput. Chem. Eng.*, : S945-S953.

Liu Z-Y (1999) Wastewater minimisation using a heuristic procedure. *AIChE Spring Meeting*, Houston. USA.

Majozi, T., (1998) The Application of Pinch Technology as a Strategic Tool for Rational Management of Water and Effluent in an Agrochemical Industry , *MScEng Thesis*, University of Natal..

Obeng, E. D. A., and Ashton, G. J., (1988), On Pinch Technology based procedures for the design of batch processes, *Chem Eng Res Des*, **66**: 255 - 259.

Olesen, S. G., Polley, G. T. (1997). A simple methodology for the design of water networks handling single contaminants. *Trans IChemE.*, **75**: 420-426.

Rossiter, A.P., Nath, R., (1995) Wastewater Minimisation Using Nonlinear Programming, Chapter 17, *Waste Minimisation Through Process Design*, A.P. Rossiter, Editor. , McGraw-Hill, New York.

Savalescu, L.E. And Smith, R., Simultaneous Energy and Water Minimisation.(1998) *AIChE Annual Meeting*, Miami Beach, Florida.

Smith, R. (1995), Wastewater Minimisation, in *Waste Minimisation Through Process Design*, A.P. Rossiter, Editor. , McGraw-Hill: New York. p. 93-107.

Takama, N., Kuriyama, T., Shiroko, K., Umeda, T. (1980). Optimal water allocation in a petroleum refinery. *Comput. Chem. Eng.*, **4**: 251-258.

Towler, G.P., Mann, R., Serriere A. J-L., Gabaude, C. M. D., (1996) Refinery Hydrogen Management: Cost Analysis of Chemically-Integrated Facilities. *Ind. Eng. Chem. Res.*, **35**: 2378-2388.

Urban-Econ, (2000), The Economic Cost Effects of Salinity, Vol. 1: Integrated Report. , *WRC Report No. TT 123/00*, Water Research Commission, Pretoria. ISBN 1 86845 590 4

Wang, Y. P., Smith, R., (1994a). Wastewater Minimisation. *Chem Eng Sci.*, **49**(7): 981-1006.

Wang, Y.P., Smith, R., (1994b) Design of Distributed Effluent Treatment Systems. *Chem Engng Sci.*, **49**(18): p. 3127-3145.

Wang, Y.P., Smith, R., (1995a) Wastewater Minimisation with Flowrate Constraints. *Trans IChemE*, **73**, Part A: p. 889-904.

Wang Y. P., and Smith R. (1995b) Time Pinch Analysis, *Trans IChemE*, **73**, Part A: 905-914.

Westerberg, A. W. (1987). Process synthesis: A morphological view. In *Recent Developments in Chemical Process Design*. 127-145, Wiley, NewYork.

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