Synthesis of an Integrated Water and Membrane Network with Multiple Electrodialysis Regenerators

by

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Declaration

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Master of Science in Chemical Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

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Abstract

The increasing cost of freshwater and wastewater treatment coupled with stringent environmental regulations has pushed process industries towards sustainable engineering, emphasising the need for water minimisation. This can be achieved through the implementation of process integration strategies such as water recycle, reuse, regeneration-recycle and regeneration-reuse between water sources, water sinks and regenerators. This concept is referred to as water allocation planning (WAP). This work addresses the WAP problem through the application of process integration and its enabling tools. A comprehensive mathematical formulation comprising of a detailed electrodialysis model that is linked to a water network model is proposed. Regeneration technologies, particularly membranes, are highly energy intensive, and hence despite being desirable should not be applied at the expense of energy. In this regard, the model developed is for the simultaneous optimisation of water and energy. The water and energy consumption terms are translated into monetary terms and the objective set to minimise the total annualised cost of the system. To demonstrate the proposed approach, the model is applied to a pulp and paper plant case study. The optimisation problem, presented as a mixed integer nonlinear programming (MINLP) problem, is solved in GAMS/DICOPT. The results indicate a potential of 12% savings in freshwater intake, 16% reduction in wastewater generated and a 14% savings in the total annualised cost for the entire network.

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CHAPTER 1

Introduction

1.1 Background

Sustainability of human activities, primarily production and consumption, has been a growing concern among all diverse groups found in society and its importance continues to be emphasised globally. Among the sustainability mega-forces, water scarcity has risen to the top of the corporate agenda for most entities in the industrial sector (Sharma & Sanghi, 2013). According to the Water Resource Group, global freshwater demand will exceed supply by 40% by the year 2030. These shrinking supplies of freshwater can disrupt business operations and the supply of key business inputs (Bartels, 2012).

In the face of these dire predictions, a number of industries are taking measures to become stewards of this vital resource. These measures include re-strategizing their operating models for businesses already in place and implementing sustainable designs for new ones. Many have managed to reduce the potentials of business disruption, cut costs and build value through innovation. However, there still exist some that fail to present a convincing picture of a thorough and robust response to this challenge (Bartels, 2012). In an effort to eliminate these discrepancies and push for the fabrication of sustainable response systems, governments are imposing strict water management laws and regulations on companies to motivate sustainable development (Judd & Jefferson, 2003) .

With particular interest in the process industry, sustainability of critical water resources relies heavily on sustainable wastewater management. According to literature, the applications of sustainability frameworks to wastewater treatment and management are very recent and limited. The basis of sustainable water management is established in the 5R policy; that is, reduction, replacement, reuse, recovery and recycle (Sharma & Sanghi, 2013).

1.2 Motivation

In this work, it is proposed that a wastewater management system based on the promotion of wastewater reuse and recycle that involves partial treatment wastewater within distributed water works could be a sound strategy for sustainable development if adopted under the right settings. Partial treatment of wastewater, also referred to as regeneration, involves a lot of technicalities that need not be disregarded as far as the benefits of regeneration are concerned. Because a plant can potentially be run at a loss when the aforementioned strategies are implemented, the optimisation of the water networks in a plant becomes a vital instrument for sustainability.

Optimisation of water networks in order to reduce freshwater intake and wastewater regeneration has been a topic for discussion for quite some time now. Various optimisation techniques have been proposed and these have been successfully implemented in water network synthesis and design. Early work focused on the conventional reuse and recycle strategies and it was only later that regeneration reuse/recycle was considered.

Extant literature has extensively covered regeneration recycle and reuse within water networks, however most studies misrepresent regeneration costs due to oversimplified assumptions incorporated within the models (Galan & Grossmann, 1999). These assumptions are made on the performance of the regenerator and the costs associated in wastewater regeneration. Membrane based separation technologies have proven very effective for partial treatment in water distribution systems. However, the most prominent (reverse osmosis and electrodialysis) are very energy intensive processes, and as such, optimisation of these processes is very important.

In light of this, the work presented in this dissertation aims to bridge the gap created by simplified regenerator models through the incorporation of detailed regenerator models within the water network model with the aim of synthesising and designing optimal water networks. Electrodialysis (ED) is considered as the regeneration technology of choice and the water network problem, modelled as a Mixed Integer Non-Linear Programming (MINLP) problem, is formulated in GAMS.

1.3 Problem statement

In this work we consider a single contaminant, integrated water network with multiple ED regenerators. Given, is:

- A set of fixed flowrate water sources j, $j \in J$, with known flowrates and concentrations of contaminants, C_j, that are amenable for recycle or reuse.
- A freshwater source, *FW*, with variable flowrate (to be optimised) and known contaminant concentration, $C_{FW,co}$.
- A set of fixed flowrate water sinks i, $i \in I$, with known flowrates requirements and maximum allowable concentration of contaminants, C^i_{max}.
- A wastewater sink, *WW*, with variable flowrate (to be optimised) and maximum allowable concentration of contaminants, C^{WW}_{max}. Wastewater that requires further contaminant removal by chemical, biological or other means go to this sink.
- A set of regenerators r, $r \in R$, of different performances in terms of the removal ratio, *RR*, and the maximum allowable concentrations in to the regenerators, C^r_{max}. Flowrate into the regenerators is variable (to be optimised). The regenerator is also characterised by the liquid recovery, α.

The objective is to synthesise and design an optimal integrated water network. The optimal configuration is one that minimises freshwater use, generation of wastewater and the capital and operating costs of both regeneration and the piping interconnections.

1.4 Structure

The rest of the dissertation is arranged as follows. First a comprehensive literature review concerning optimisation of water networks is presented. Secondly a chapter on the development of the optimisation model is presented. Thereafter the results of applying the proposed model to a case study are presented and discussed. Recommendations on future work in the field are suggested in the subsequent chapter and finally conclusions in relation to the consequences of the findings are made in the last chapter.

1.5 References

Bartels, W., 2012. Water Scarcity: A dive into global reporting trends: KPMG International Cooperative.

Galan, B. & Grossmann, I. E., 1999. Optimisation Strategies for the Design and Synthesis of Distributed Wastewater. *Computers and Chemical Engineering Supplement*, pp. S161-S164.

Gunaratnam, M. et al., 2005. Automated Design of Total Water Systems. *Industrial and Engineering Chemistry Research*, Volume 44, pp. 588-599.

Judd, S. & Jefferson, B., 2003. *Membranes for Industrial Wastewater Recovery and Re-use*. Oxford, UK: Elsevier Ltd.

Sharma, S. K. & Sanghi, R., 2013. *Wastewater Reuse and Management*. London: Springer Science + Business Media Dordrecht.

Takama, N., Kuriyama, T., Shiroko, K. & Umeda, T., 1980.Optimal Water Allocation in a Petrochemical Refinery. *Computers and Chemical Engineering*, Volume 4, pp. 251-258.

Yang, L., Salcedo-Diaz, R. & Grossmann, I., 2014.Water Network Optimisation with Wastewater Regeneration Models. *Industrial & Engineering Chemistry Research*, 22 September, Volume 53, pp. 17680-17695.

CHAPTER 2

Literature Review

2.1 Introduction

The work in this dissertation concerns the optimisation of water networks. As such, relevant literature that covers this field is considered in this chapter. First, a background and motivation for the optimisation of water networks is presented. Then, optimisation strategies and their strengths and limitations are reviewed giving reference to published work. Finally, a detailed discussion on water regeneration is given, paying particular attention to electrodialysis regeneration which is the technology of choice for the current study.

2.2 Industrial Water Management

Industrial water uses include processing, cooling/heating, cleaning, transporting and flushing of waste and it is these operations within a plant that determine, both quantitatively and qualitatively, the water demand and wastewater generated. Industrial freshwater supplies include rivers, dams, groundwater and municipal water whereas disposal sites include rivers and sewers. While the sector grows globally, there has been high pressure on freshwater supplies and as environmental regulations on wastewater disposal become more stringent, the rise in freshwater costs as well as effluent treatment costs have become more noticeable. As such, the process industry has been incentivised to reduce freshwater intake and wastewater generation so as to maintain plant profitability (Kuo & Smith, 1998).

Water minimisation schemes applicable to the process industry include recycling, reuse, regeneration-recycle and regeneration-reuse. Regeneration refers to the partial treatment of water before recycle/reuse. Figure 2.1 illustrates these schemes. Statistics show that approximately 22% of water consumed globally is used by the industrial sector and it is assumed that, for plants lacking water recycle/reuse schemes or treatment facilities, about 85% to 96% of the water consumed in plant operations comes out as wastewater (Sachidnanda & Rahimifard, 2012). According to Sharma and Sanghi (2013), water recycling and reuse have the potential of generating higher water savings in industry than in agriculture and domestic consumption. As such focus has shifted from only using the conventional end-of-pipe water treatment strategies to incorporating the aforementioned schemes for industrial water management.

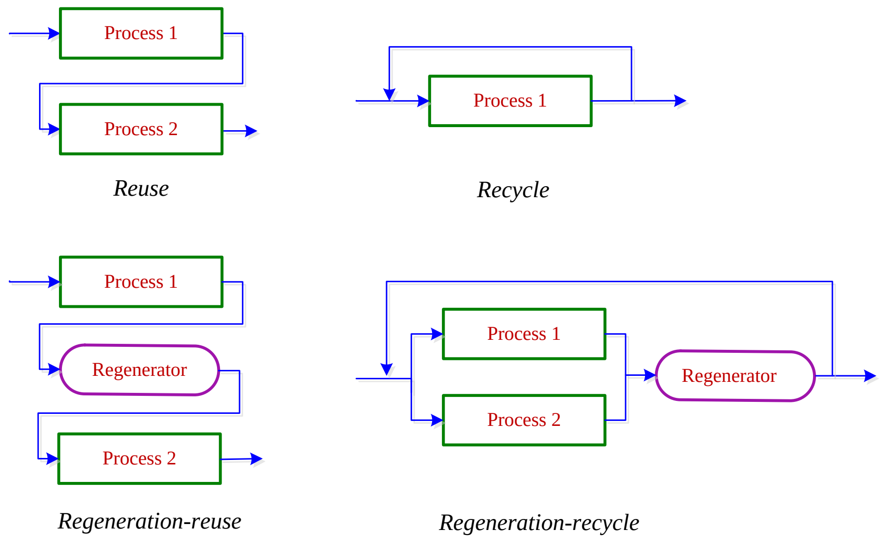


Figure 2.1: Water minimisation schemes.

According to Bagajewicz (2000), extensive application of these schemes may lead to 'zero liquid discharge'. This refers to the concept of a closed system where water disposal is eliminated altogether. This minimises the consumption of freshwater to that required for make-up (Lavric et al., 2005). A closed circuit is appealing because it eliminates the administrative costs associated with final waste disposal. Although unrealistic from a practical point of view, the concept presents the ultimate goal for green water utilisation that both academia and industry attempt to achieve.

2.3 Process Integration

There exist quite a of number studies where resource management problems are decomposed into subproblems such that the interactions between the different parts are not simultaneously explored (Alva-Argaez et al., 1998; Karuppiah & Grossmann, 2006). The motive for this notion being the need to avoid handling complex interactions between subsystems (Chang & Li, 2005). The same idea was inherent in the early works on water minimisation studies (Huang et al., 1999). Examples include work by El-Halwagi and Manousiouthakis (1989), Gupta and Manousiouthakis (1994) and El-Halwagi et al. (1996), all of which used sequential design strategies.

Process integration is a holistic approach to process design, retrofitting and operation that emphasises the unity of a process by virtue of the strong interactions that exist between the different unit operations (El-Halwagi, 2012; Tan et al., 2009). As far as sustainability is concerned, process integration is a powerful and effective framework for sustainable design. It concerns the minimisation of resource consumption through designing and planning utility networks within industrial manufacturing plants under a unified framework (Tan et al., 2009). As mentioned earlier, by means of process integration, water minimisation can be achieved through water recycle, reuse as well as regeneration-recycle and regeneration-reuse.

Increased economic and environmental awareness in relation to sustainable engineering has driven designers toward more efficient water systems through process integration (Huang et al., 1999). In this regard, the optimisation of water networks has become a vital instrument of sustainability as it allows extensive exploration of the synergies that exists between water-using operations and water treatment systems to ensure their efficient integration. Water management through these techniques has grown to be a mature field where complex conditions are analysed and solved.

2.4 Water Allocation Planning (WAP)

The concept of reusing and recycling water to minimise freshwater intake and wastewater generation while processes receive water of adequate quality is referred to as the water allocation planning (WAP) problem (Bagajewicz & Savelski, 2001). The objective is to synthesise a network that integrates the water-using processes with the regeneration operations by optimisation.

The basic elements of a WAP problem comprises of water sources and sinks, treatment units, splitters and mixers. In order to solve the design problem, limiting data for the operations considered need to be available (Jezowski, 2010). This includes limits on the inlet and outlet concentration of contaminants as well as limits on the fixed load of contaminants for each operation. Connectivity between the elements by means of piping, allows water minimisation through recycle/reuse and regeneration recycle/reuse to be achieved.

Identifying and deploying the best water reuse systems is a challenge. Modern technologies present numerous complex alternatives that the designer must consider and as such, techniques to be used to determine optimal water reuse strategies have been proposed. Approaches to solving the WAP problem can be broadly divided into two, namely insight-based (conceptual) and mathematical programming (systematic) approaches.

2.5 Insight-Based Techniques

2.5.1 Background

Insight-based optimisation techniques evolved directly from heat pinch and mass integration techniques (Rangaiah & Wei, 2010). Insight-based techniques, primarily water pinch provide physical insights into which part of the problem requires more accurate data than the other. Additionally, candidate operations for change to allow targets to be improved as well as areas where regeneration is likely to be beneficial can easily be identified (Doyle & Smith, 1997).

Pinch analysis refers to a rigorous, structured approach that can be useful in tackling problems related to process and site utilities and therefore presents opportunities for reducing operating costs and capital investment, debottlenecking processes and improving efficiency. The concept analyses a commodity, in this case water, in terms of its quality and quantity and recognises the fact that the cost of using the commodity will be a function of both. The fundamental principle behind the approach is to match individual demand for a commodity with a suitable supply, depending on the quality required and the quality offered (CanmetENERGY, 2003).

Most of the early water pinch techniques were based on iterative targeting which concerns the use of multi-step graphical approaches to evolve the usage of freshwater into a minimum target (El-Halwagi et al., 2003). Later approaches, involved detailed network designs that are based on the matching of water sources and demands and determining the configuration of a network that provides minimum freshwater targets.

2.5.2 Mass-transfer Based Water Pinch

Wang and Smith (1994a), proposed the first water pinch approach for the minimisation of water in process plants. Using concepts from heat exchange networks and mass-exchange networks, the method starts by developing limiting water profiles for each of the unit operations considered in the plant. Each profile indicates the limiting case when the minimum water flowrate is used by a unit; that is, when the maximum inlet and outlet water concentrations are specified. Figure 2.2 graphically illustrates a limiting water profile for a typical process.

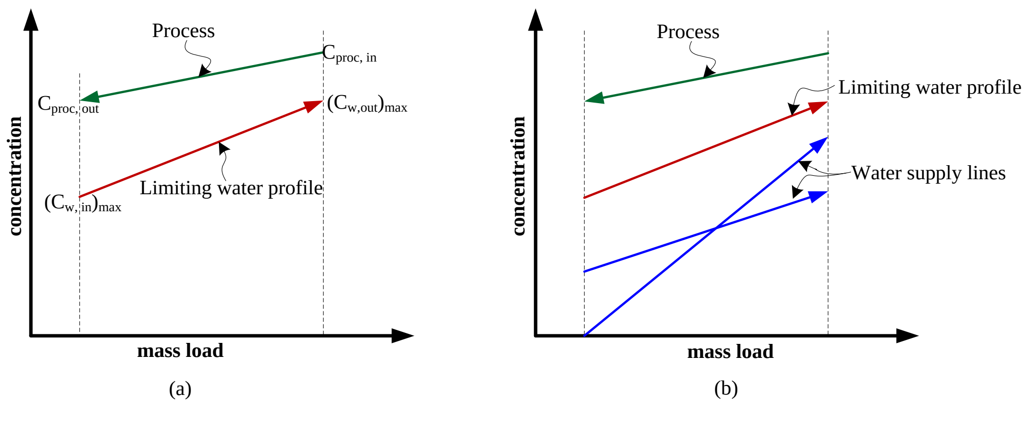


Figure 2.2: Typical water limiting profiles.

Any water supply line below the limiting profile line satisfies the requirements for the given process as depicted by Figure 2.2. The limiting data for each unit is determined based on:

i. mass transfer behaviour
ii. solubility limits
iii. need to avoid precipitation
iv. fouling and corrosion limitations
v. flowrate limit to avoid solid material settling

To incorporate the holistic nature of process integration, individual profiles are combined to form a limiting composite curve which represents the overall water sources (flowrate and concentration) available on the plant, as well as the water sinks. The minimum fresh water flowrate through the overall process is determined by matching the overall freshwater supply line against the limiting composite curve as shown in Figure 2.3. According to Figure 2.3 the water supply line touches the limiting composite line at an intermediate point called the 'pinch point'.

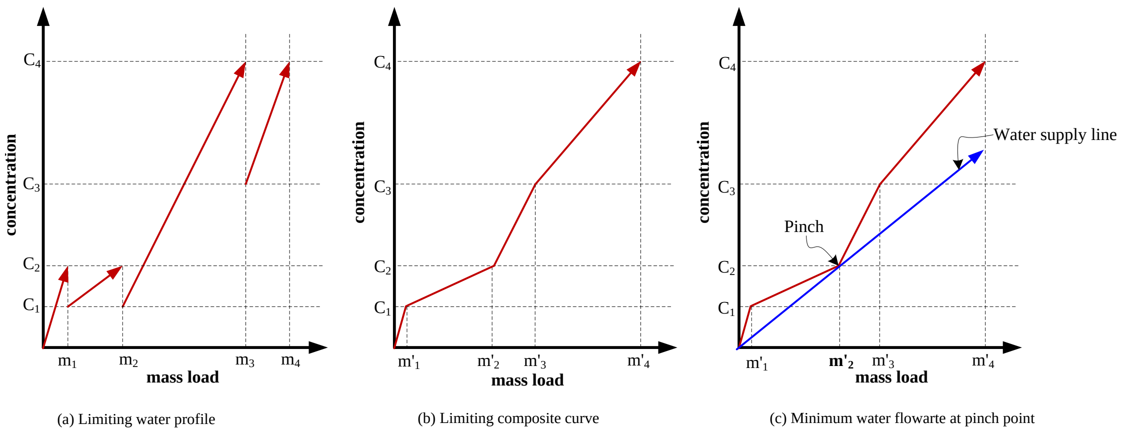


Figure 2.3: Limiting composite curves.

The water pinch indicates the bottleneck for further water minimisation. Operations below the pinch require freshwater and those above the pinch can reuse water from other operations. To decrease the usage of water further, only processes under the pinch point need to be considered (Wang & Smith, 1994a). After the targeting step, some rules are used to derive a set of alternative network design structures. In practice, each of the networks obtained is evaluated for its applicability and the best one is chosen.

Using this basic approach, Wang and Smith (1994a) tackled cases for single and multiple contaminants. Options for wastewater regeneration were also explored. The authors observed that the approach led to designs with unnecessary complexity and as such they modified it to produce alternative water network designs that exploit by-passing and mixing to minimise the number of recycle/reuse matches (Wang & Smith, 1994a). Noteworthy is that in their approach, freshwater targets are set before the water network is designed.

Later, Wang and Smith (1994b) presented a method for the design of distributed effluent treatment systems using pinch technology. The approach was very similar to that by Wang and Smith (1994a). The work aimed at minimising the flowrate of effluent to be treated, under the assumption that cost is minimised when the quantity of wastewater to be treated is minimised. As such, the treatment flowrate was the target flowrate and instead of having a composite limiting curve, they had a composite effluent curve. Based on the analysis of their results they managed to set design rules, specifically for targets to be achieved in practice based on the location of the pinch point. Streams starting below the pinch completely bypass treatment and those above, are fully treated, while those starting at the pinch are partially treated.

Despite being able to provide useful insights into the design of distributed effluent systems, for some instances, the method by Wang and Smith (1994b) fails to give minimum targets for treatment flowrates because it is the network structures that are optimised not the targets. Additionally it failed to address important design features when using multiple regenerators as all the design structures that emerged from the method were always connected in series.

In light of these limitations, Kuo and Smith (1997) improved the technique by considering optimisation costs that are based on the targets instead of the individual designs. This was achieved by subjecting the initial design to detailed simulation and costing after which the design is either approved or iterated back to the targeting and network design. They also further extended the approach to handle retrofitting cases.

It was the pioneering work of Wang and Smith (1994a) that stimulated a series of enthusiastic research activities in the field of water pinch. Since their work, heuristics and somewhat similar graphical and tabular schemes have been amalgamated into water pinch to refine and modify the technique and extend its applicability to various systems found in the real world. This includes the water mains method by Kuo and Smith (1998) which involved pinch identification, operation grouping and operation migration. This method can sharply reduce freshwater consumption; however, it does not guarantee optimal solutions (Teles et al., 2008).

2.5.3 Non-Mass Transfer Based Water Pinch

Noteworthy is that all the water pinch techniques discussed thus far are based on a mass transfer model. As such, units such as reactors, boilers and cooling towers that are concerned with flowrate only and not the amount of contaminant transferred cannot be modelled adequately in a similar way. Moreover the early method could not handle cases of several aqueous streams entering a unit as well as water gains and losses which are very common in practical operations.

In response to these limitations, Dhole et al. (1996) developed a new technique that overcame these difficulties; however, the technique was not purely graphical. In the approach, network designs are first developed using mathematical programming and then graphical representation of the designs are developed afterwards (Hallale, 2002). Details of the technique are discussed later.

Later, Hallale (2002) adapted ideas from Dhole et al. (1996) to develop a new graphical targeting approach. Unlike the method proposed by Dhole et al. (1996), this technique is purely graphical and therefore gives water targets *a priori*, not the design (Hallale, 2002). In this approach, demand composite and source composite are plotted on fractional water purity (vertical) versus flowrate (horizontal) axes, hence the plots are made up of horizontal and vertical lines as illustrated in Figure 2.4.

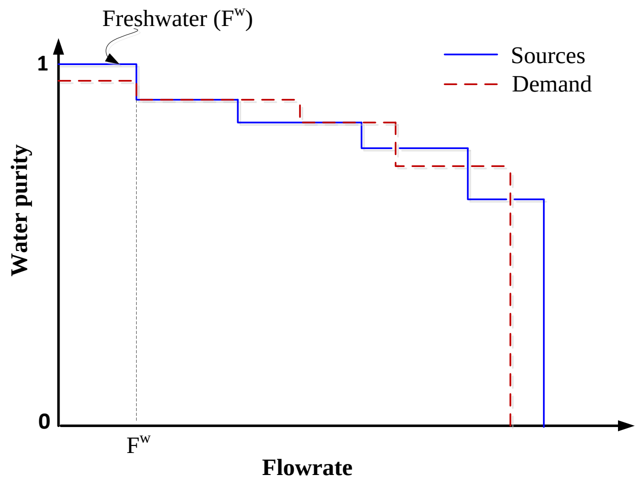


Figure 2.4: Construction of demand and source composites.

A freshwater flowrate is arbitrarily assumed and included in the source composite. The technique examines this assumed freshwater flowrate for feasibility by means of water surplus diagrams. These are constructed noticing that at some regions the source composite is above the demand composite implying a surplus of pure water and vice-versa. The pure water surplus and deficit at each region is determined by calculating the area of the enclosed rectangles. The cumulative surplus is plotted against the water purity to form the water surplus diagram. Figure 2.5 shows how the water surplus diagram is constructed.

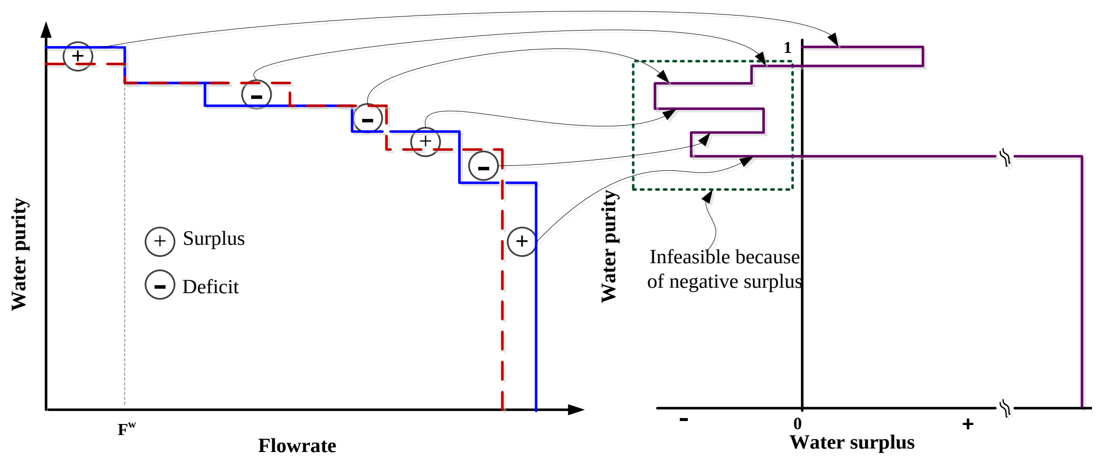


Figure 2.5: Construction of a Water Surplus Diagram (Hallale, 2002).

Because cumulative surplus is enclosed between the two composites in an integral function, the approach automatically incorporates the possibility of mixing sources. If part of the plot lies on the negative side, it implies that there is insufficient purity and more freshwater has to be added until no part of the surplus diagram is negative. The procedure is repeated until the minimum freshwater and wastewater targets are achieved; that is when the plot just touches the vertical axis as shown in Figure 2.6.

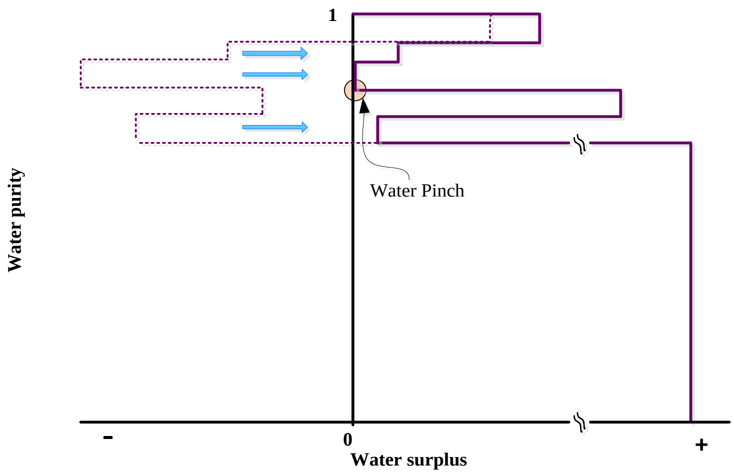


Figure 2.6: Determination of minimum water targets.

The targeting problem is linear and can be obtained using mathematical programming to attain a global optimum; however, the graphical technique offers increased insights on beneficial process modifications and regeneration (Hallale, 2002). Once the target has been set, a set of network designs is developed and the best one chosen based on economic, geographical and safety constraints.

The major drawback in the method proposed by Hallale (2002) was the extensive calculations required to produce surplus diagrams. In view of this El-Halwagi et al. (2003) developed a new single-stage, systematic and graphical targeting technique for recycle/reuse networks building on from the work of Dhole et al. (1996) and the ideas presented by Hallale (2002). In their method, optimality conditions were first established using dynamic a programming formulation and parametric optimisation. The results of applying the conditions are then used in developing a pinch-based graphical representation of composite load versus flowrate (El-Halwagi et al., 2003).

Manan et al. (2004) developed a new systematic numerical alternative to water surplus diagrams referred to as the water cascade analysis (WCA). This tabular technique eliminates the tedious iterative procedure of the water surplus diagrams and allows for quick and accurate determination of water targets as well as assessments for regeneration opportunities and process changes. According to Manan et al. (2004), a good targeting technique to determine true minimum targets should:

i. handle both mass-transfer based and non-mass-transfer based water operations
ii. consider both flowrate and concentration driving force (water purity) for water reuse
iii. be noniterative and yield exact targets

The method uses an interval water balance table to determine net water source/demand at each level. Cumulative net water source/demand is obtained from water cascading and then is used to determine minimum water targets. Manan et al. (2004) showed that water cascade analysis is a numerical equivalent of the water surplus method by Hallale (2002). The method is capable of generating exact utility targets and pinch location more quickly. To date, this technique has been applied successfully in industry and continues to be used (Ng et al., 2007).

2.5.4 Limitations of Pinch

Despite the success in achieving minimum water targets, water pinch has the limitation of failing to obtain high accurate targets because of its graphical nature. Additionally, the method fails to consider multiple contaminants simultaneously (Hallale, 2002) and as the problem becomes bigger, that is; multiple contaminants, multiple sources and sinks and multiple treatment processes, the technique becomes tedious and less accurate (Kuo & Smith, 1997). It was also observed that a lot of the early water pinch methods struggle to deal with multiple pinches and retrofitting cases although the later methods manage such situation relatively well (Hallale, 2002; Manan et al., 2004).

Another major limitation of water pinch is its inability to incorporate all constraints of the problem. As highlighted by Doyle and Smith (1997), water minimisation problems are not confined to concentration and flowrate constraints only. Other constraints such as economic, geographical and safety constraints also exist and these affect the optimal designs to be considered. Additionally, cost constraints determine the economic feasibility of a design. However, most water pinch methods do not guarantee cost optimal solutions (Doyle & Smith, 1997). A true robust method needs to consider all these constraints however complex they may be.

2.6 Mathematical Programming

2.6.1 Background

Mathematical programming was inspired by the many limitations of using insight based approaches, primarily the need to eliminate the tedious steps of graphical targeting and to incorporate all constraints into the problem. It often applies superstructure optimisation which involves the use of a representation of all possible solutions to the problem (Jezowski, 2010). Based on this superstructure, a mathematical model, describing the problem with all economic, geographical, control and safety constraints included, is built. This enables the technique to deal with more detailed design considerations such as data uncertainties, life-cycle impacts, network topology and capital costs (Tan et al., 2009). The optimisation problem represented as a mathematical model is then solved using rigorous algorithms to obtain global or near-global solutions. Minimum water targets are determined simultaneously with the network design.

Within mathematical programming, problems can be modelled using either fixed contaminant mass-load framework or fixed flowrate framework. Fixed mass load operations are quality controlled and their data is usually expressed by limiting flowrate and maximum inlet and outlet concentrations (Bandyopadhyay & Cormos, 2008). Outlet concentrations on units are dependent on the inlet concentrations and flowrate; however, inlet and outlet flowrates are assumed to be the same (Teles et al., 2008).

On the other hand, fixed flowrate operations are quantity controlled. They can be used to model both mass transfer based operations and non-mass transfer operations (Bandyopadhyay & Cormos, 2008). A unit is treated either as a water source or as a wastewater sink with fixed output and input flowrates, respectively. A fixed contaminant concentration for the sources is specified as well as the concentration upper limits to the sinks' inlets. Inlet and outlet flowrates need not be equal therefore the outlet concentrations are independent of the inlet concentrations (Teles et al., 2008).

Literature shows that operations under a fixed flowrate framework are more prominent than those under a mass load framework and as such, have become more attractive compared to fixed-load models. They can be applied to various situations, in miscible phase networks, water allocation in industrial parks, in urban water networks as well as in some mass-transfer based operations that require a fixed flowrate framework (Bandyopadhyay & Cormos, 2008; Poplewski et al., 2010).

Trends similar to those observed in the development of water pinch in terms of which framework to adopt have been observed in the development of mathematical programming techniques. Early approaches were mostly mass-load based while the later methods shifted towards a fixed-flowrate framework (Khor et al., 2014). The decision of which framework to adopt depends on the author's opinion and the availability of data.

2.6.2 Convexification

Generally, superstructure optimisation models are nonlinear in nature, owing to the large number of economical, topological, component and mass balance constraints associated with them (Bagajewicz & Savelski, 2000). As such, most optimisation problems result in complex nonlinear programming (NLP) problems or mixed integer nonlinear programming (MINLP) problems that are usually nonconvex and difficult to solve to global optimality. Figure 2.7 shows a general overview of the problem types related to optimisation problems. Standard NLP and MINLP solvers do not guarantee global optimality for nonconvex problems.

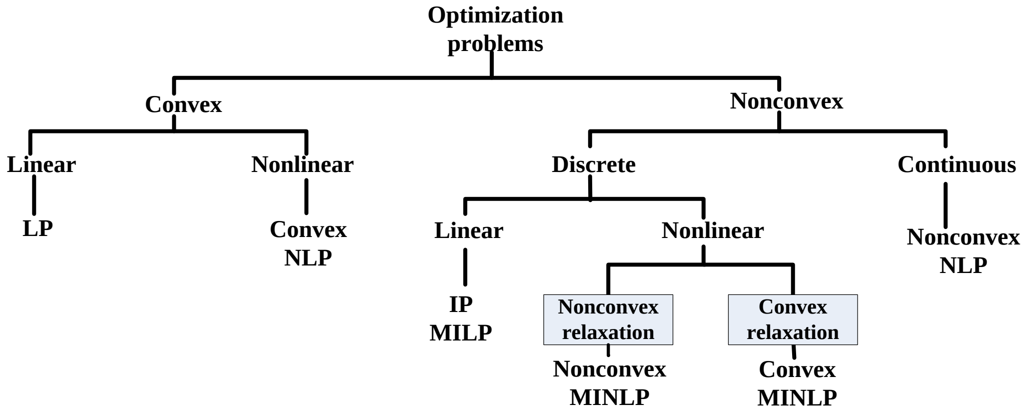


Figure 2.7: Problem types related to optimisation problems (Lin et al., 2012).

Algorithms and procedures aimed at solving nonconvex problems target developing convex underestimators (approximations of the nonlinear formulations) to formulate lower bounding convex NLP/MINLP problems that can be solved to global optimality using standard solvers (Grossmann & Biegler , 2004). Figure 2.8 illustrates a typical convex underestimator to a nonconvex function. These convexification methods achieve this either by directly replacing each nonconvex function with a convex underestimating function or by introducing new variables (transformations) and convex constraints that accurately approximate the nonconvex function (reformulation-convexification). These relaxation techniques form the main ingredients of most of the existing exact algorithms for nonconvex NLP and MINLP problems.

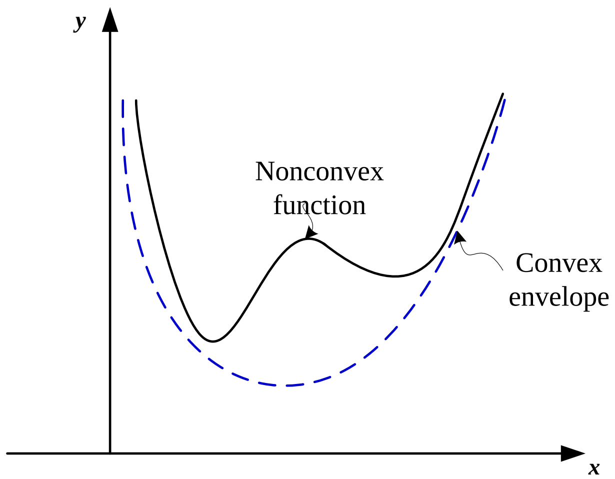


Figure 2.8: Convex envelope for a nonconvex function.

2.6.2.1 Convex relaxations

For general continuous and differentiable nonlinear functions a general approach for underestimation is to add a quadratic term that, when sufficiently large, underestimates the original nonconvex function (Grossmann & Biegler , 2004). McCormick (1976), proposed a general approach for deriving underestimator functions (convex envelopes) for bilinear and linear fractional terms that can be incorporated into global optimisation algorithms. According to McCormick (1976), for each bilinearity, $w_{ij} = x_i \cdot x_j$ the following constraints are introduced.

$$
\begin{aligned}
w_{ij} &\geq x_i \cdot x_j^L + x_i^L \cdot x_j - x_i^L \cdot x_j^L \\
w_{ij} &\geq x_i \cdot x_j^U + x_i^U \cdot x_j - x_i^U \cdot x_j^U \\
w_{ij} &\geq x_i \cdot x_j^L + x_i^U \cdot x_j - x_i^U \cdot x_j^L \\
w_{ij} &\geq x_i \cdot x_j^U + x_i^L \cdot x_j - x_i^L \cdot x_j^U
\end{aligned} \tag{2.1}
$$

This relaxation gives a lower bound on a problem. However, this lower bound can be weak depending on the bounds on x_i and x_j which can be improved using the convex envelopes on discretised portions of the variable range, a method called piecewise linearisation. The method has been used extensively in literature for many optimisation problems (Galan & Grossmann, 1999; Khor et al., 2014).

Most convex relaxation methods that have been successfully implemented involve a reformulation step before the problem is actually convexified. The common reformulation strategies are factorisation and block separability. Factorisation or factorable programming relaxation involves the introduction of additional variables and constraints such that the resulting nonlinear problem involves functions of a simpler form. In this way, only the under and overestimators of the simple form are required. According to McCormick (1976), just about any function used for computational purposes can be put into a factorable programming problem.

Block separability is the key structural property that is exploited by decomposition-based relaxation methods (Nowak, 2005). A function $f(x,y)$ is separable if there exist functions $g(x_i)$ for $i=1,\dots,n_1$ and $h(y_i)$ such that:

$$f(x,y)=\sum_{i=1}^{n_1} g(x_i)+\sum_{i=1}^{n_2} h(y_i) \tag{2.2}$$

Separable relaxation involves the use of piecewise under and over-estimators in which convex under/overestimators for all the $g(x_i)$ and $h(y_i)$ are determined. If convex underestimators for each of the functions are summed up, they result in a convex underestimation of the function $f(x,y)$. Even for cases where useful underestimators are not available, each of the sub-functions are approximated with linear piecewise functions. This involves the addition of new continuous variables for the two functions and binary variables for each piecewise linear function. In this way, any nonconvex MINLP with separable functions can be approximated by a convex MILP.

Linear relaxation methods employ a reformulation-linearisation strategy to yield a linear programming problem whose solution provides a tight envelope to the original nonconvex problem. In this method, the signomial functions (functions with bilinear and trilinear terms), are first reformulated and then convexified using valid transformations which convert the nonlinear functions into linear functions (Nowak, 2005).

For linear relaxation methods the linearisation is usually done using McCormick convex envelopes. Glover (1975) also proposed a set of exact transformations that can effectively linearise the bilinearities resulting from the multiplication of a continuous variable with a binary variable. The Glover transformations seek to alleviate the customary blow up in size due to the addition of new variables and constraints that often occurs when using the other linearisation techniques (Glover, 1975).

Sherali and Alameddine, (1992) proposed the first reformulation-linearisation technique for bilinear programming that is designed to exploit special structures of the problem. In their method, the problem is first reformulated to generate additional valid nonlinear constraints that can be effectively linearised by defining a new set of variables, one for each nonlinear term.

Quesada and Grossmann (1995) implemented the principles of the technique to obtain a novel linear relaxation for use in a branch and bound algorithm. Galan and Grossmann (1998) and Karuppiah and Grossmann (2006) successfully used a similar linearisation technique. Meyer and Floudas (2005) and Misener and Floudas (2010) proposed a new piece-wise reformulation-linearisation technique and applied it to a class of pooling problems that is important to process industries.

For other convex relaxation methods, convexification is carried out using other transformations which need not be linear. Valid transformations that can be used in addition to McCormick (1976) and Glover (1975) include power, inverse and exponential transforms. Convex under and overestimators for concave univariate, bilinear and linear fractional functions have also been developed by Quesada and Grossmann (1995) and Zamora and Grossmann (1998). A comprehensive study on the different transformations available has been presented by Lundell (2009). The relative effectiveness of a transformed approach depends on the problem at hand. Various authors have addressed the issue on how best to choose transformations appropriate for a given problem while others have developed ways of optimising a set of transformations to be used in a problem (Lundell & Westerlund, 2008)

Lundell and Westerlund (2012), utilised a reformulation technique for MINLP problems (containing non-convex twice differentiable functions) that used the solution of an MILP problem as the minimal set of transformations. For positive signomial terms, the positive power transform, the exponential transform and the mixed power exponential transform were considered. For negative signed terms, the power transformation and the alpha-BB reformulation (a quadratic function is added to a non-convex function resulting in a convex underestimator) was considered. These transformations convexify a problem and overestimate its feasible region in an extended variable-space.

Pörn et al. (1999), proposed a convexification strategy for posynomial and negative binomials in discrete optimisation problems. This is achieved by applying potential and exponential transformations to nonconvex functions. Later on, Pörn et al. (2008) developed a convexification strategy that made use of exponential and inverse transforms. Exponential and inverse transforms were considered for positively signed terms while for negatively signed terms potential transforms were used. To avoid the problem of multiple local optima brought about by nonlinear equality constraints, a discretisation (piecewise linear reformulation) scheme was proposed. Both techniques have been successfully incorporated in the extended cutting planes algorithm for MINLP problems.

2.6.3 The techniques

Different algorithms and solution procedures for optimisation problems have been proposed and these fall within five general classes, namely:

i. direct linearisation,
ii. generation of good starting points,
iii. sequential solution procedure,
iv. stochastic optimisation approach and
v. deterministic optimisation

These will be discussed in the subsequent sections.

2.6.3.1 Direct linearisation

Direct linearisation techniques are based on the development of a linear programming (LP) formulation for the water network problem. Rules of thumb for the existence of linearity are assumed to linearise the problem directly and these have been presented in literature (Jezowski, 2010). Bagajewicz and Savelski (2000), Bagajewicz and Savelski (2001) and Salveski and Bagajewicz (2003) presented necessary conditions of optimality valid for freshwater minimisation. These conditions had already been applied in previous work, but without proof. According to these conditions a solution to the WAP problem is optimal if:

i) for a single contaminant model, the outlet concentration of a process is not lower than the concentration of the combined wastewater streams coming from all the precursors.
ii) for a single contaminant model, the outlet concentration of a head (H), intermediate (I) and terminal (T) process reach their maximum (Bagajewicz & Savelski, 2000).
iii) for a single contaminant model with regeneration capabilities, the outlet concentration of the regenerator is the minimum possible(Bagajewicz & Savelski, 2001).

iv) for a multi-contaminant model, the outlet concentration of a key compoent is not lower than the concentration of the combined wastewater streams coming from all the precursors.

v) for a multi-contaminant model, the outlet concentration 'key' contaminant of a head (H), intermediate (I) and terminal (T) process reach their maximum.

vi) for a multi-contaminant model, the outlet concentration of at least one contaminant of an intermediate (I) or terminal (T) process reaches its maximum (Salveski & Bagajewicz, 2003).

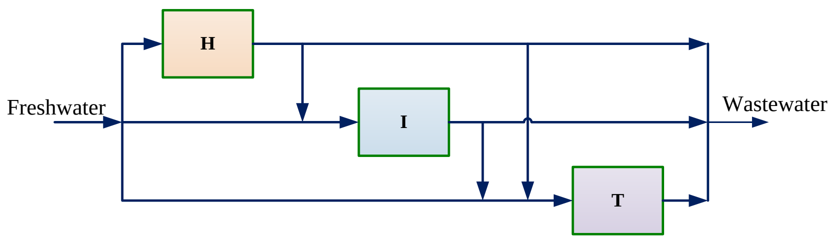


Figure 2.9: Schematic representation of a water network.

Figure 2.9 defines the head (H), intermediate (I) and terminal (T) processes. According to Lavric et al. (2005) these conditions reflect unique cases of the principles of driving force equipartition along a process which ensures minimum entropy generation for the given operating conditions. This is a measure of process irreversibility.

Bagajewicz and Savelski (2001) and Bagajewicz et al. (2000) made use of the direct linearisation technique on a mass-transfer based single-contaminant water allocation problem by applying these conditions. Assuming these conditions enables the elimination of bilinearities in the respective equality constraints thereby directly linearising the nonlinear problem. The problem was solved for minimum freshwater intake, minimum number of interconnections and minimum total fixed costs (Bagajewicz & Savelski, 2001).

In a follow-up study, Salveski and Bagajewicz (2003) tackled a multi-contaminant case by applying the respective assumptions for optimality. The technique adopted by the authors introduced a tree searching algorithm with efficient branch cutting criteria that generates all possible sequences of water-using operations from which the best one (maximum reuse structure) is chosen. The same linearisation technique was used by Koppol et al., (2003), to demonstrate the applicability of the technique to different industrial case studies.

Walczyk and Jezowski (2008) directly linearised a water network problem by following the concepts of Salveski and Bagajewicz (2003) and also applying some novel logical conditions. The logical conditions were used for selecting the water using operation parameters from among three heuristically selected conditions. Their approach does not require any branching schemes as the logical conditions eliminate the need to generate a maximum reuse structure. Although the technique does not guarantee a global optimum, near global optimum results can be attained in very short CPU times (Walczyk & Jezowski, 2008). Literature suggests the method can be improved by using a local nonlinear programming solver (Jezowski, 2010).

2.6.3.2 Generation of a good starting point

Initial guesses adopted by NLP and MINLP local solvers always have a profound impact on the convergence process towards the optimum solution (Li & Chang, 2007). The strategy of generating a good starting point is an initialisation technique that determines good starting points to be used for optimisation, typically for deterministic and stochastic optimisation. Usually, starting points are obtained through apparent robust stochastic methods or problem linearisation. However, some of these techniques produce sole starting points that can trap local solvers into sub-optimal solutions and compromise the quality of the solution (Teles et al., 2008). With good starting points, a local optimiser can obtain optimum results in fairly short CPU times (Poplewski & Jezowski, 2007).

Within the water minimisation framework, the method of generating a good starting point has been mostly applied on mass-transfer based problems and the general rule of thumb is to fix process outlet concentrations to their maximum values (Teles et al., 2008). The technique is usually applied on wastewater treatment network problems as these require feasible starting points to obtain global or near global solutions hence fine problem initialisation techniques have to be adopted. For most cases, the technique proposes applying reduced superstructures which are sequential arrangements of the available treatment operations (Jezowski, 2010).

Poplewski and Jezowski (2007) applied the initialisation technique to a stochastic random search for an optimal wastewater treatment network design. Based on the technique, they established that all possible centralised treatment network configurations constitute feasible starting points for the design of the treatment networks. Literature reports that other studies that applied this technique have also established other specific and more involved settings to obtain desired initial points (Jezowski, 2010).

Li and Chang (2007) developed an efficient initialisation strategy to be successfully applied on the synthesis of optimal water network designs. The approach makes use of limiting data for the operations under consideration as well as the necessary conditions of optimality as presented by Salveski and Bagajewicz (2003). Li and Chang (2007) proved that when an effective initialisation technique is used even for the difficult MINLP models, shorter computational times are achieved.

Teles et al. (2008) proposed novel initialisation techniques capable of generating multiple starting points that correspond to feasible networks for the design of water networks without treatment systems. The method approximates the general NLP by solving a sequence of linear programming (LP) subproblems to obtain the multiple starting points (Teles et al., 2008). Other researchers have also used fairly similar initialisation techniques that have proved successful for water network optimisation. (Poplewski & Jezowski, 2007)

2.6.3.3 Sequential solution procedure

The sequential solution procedure involves the decomposition of the overall problem into a series of simpler subproblems. The subproblems are solved in a progressive manner until an acceptable solution to the original problem is obtained (Li & Chang, 2007). The techniques usually begin with an initialisation procedure to produce feasible starting points. Solving the problem may involve relaxation techniques and the addition of extra constraints to enhance convergence (Jezowski, 2010).

Takama et al. (1980) was the first to address the WAP problem using this approach. By successively employing a penalty function, the NLP problem was transformed into a series of subproblems without inequality constraints thereby successively reducing the system structure. Feasible initial points were generated by successively modifying the penalty function. The objective to minimise the total annualised cost was carried out and solved using the Complex method (Takama et al., 1980). According to Alva-Argaez et al. (1998), this solution strategy results in topology traps due to the arbitrary decisions made and is therefore unreliable. Despite these shortcomings, the approach provided a starting point for other proposals as it was the pioneering work that applied optimisation to water network synthesis (Jezowski, 2010).

In a follow-up study to eliminate the problems encountered by Takama et al. (1980), Doyle and Smith (1997) used a sequential method that combined LP and NLP optimisation in an iterative procedure to tackle the water minimisation problem. The authors adopted the superstructure used by Takama et al. (1980). The method starts with an initialisation step where a linear formulation is used to find a starting point for the nonlinear problem. The problem is then solved using standard non-linear optimisation solvers like a successive quadratic programming (SQP) solver. Literature reports that the solutions obtained through this procedure may be suboptimal because of premature decisions made in the initialisation stage (Li & Chang, 2007).

In a somewhat similar approach, Guanaratnam et al. (2005) decomposed an MINLP problem into MILP and LP subproblems to initialise the problem and then the design was fine-tuned using an MINLP algorithm. The method starts with a relaxation procedure for the material balances to form an MILP formulation. Solution of the MILP subproblem gives an initial point for an LP subproblem which in turn provides data for the MILP in the next MILP-LP sequence. The procedure terminates when the convergence criteria is met (objective function of LP problem is reduced to a tolerance limit) and the solution is used as a starting point for the MINLP problem. According to Gunaratnam et al. (2005), the technique does not guarantee global optimality and therefore should be viewed as a decision support tool to eliminate alternatives. Similar LP-MILP model solution sequences have been reported in literature for the synthesis of wastewater treatment networks (Alva-Argaez et al., 1998; Alva-Argàez et al., 2007).

2.6.3.4 Stochastic optimisation (Meta-heuristics)

The stochastic optimisation approach is characterised by the use of physical analogies to create random points that mimic a progression towards an equilibrium condition

(Grossmann & Biegler , 2004). It is a viable modelling tool for long-term water resources management because it directly integrates uncertainties into the optimisation framework, enabling its optimal solution to better curtail possible future uncertainties. Because of its random nature, the technique encompasses a vast number of problem settings reflecting the problem at hand. Within water network optimisation, genetic algorithms have been used for water network design and adaptive random search techniques for both water network and wastewater treatment network designs (Jezowski, 2010).

The technique may involve the use of simple heuristic rules that depend on the objective function and the constraints. It is highly dependent on problem initialisation which can be determined through meta-heuristics, linearisation or the method of generating a good starting point (Jezowski, 2010). Because equality constraints are difficult to handle for most stochastic techniques, the technique often involves the application of augmented goal functions with proper penalty terms or the direct solution of equalities in a sequential manner (Poplewski & Jezowski, 2007).

Genetic algorithms are nature based and inspired by the principle of natural selection which tries to retain genetic information from generation to generation. It starts with a heuristic initialisation step and then an iterative procedure that uses genetic manipulations to obtain the optimum results. Using this technique, Lavric et al. (2005) managed to generate an overall optimal water network topology, with all restrictions being fulfilled. Because of its stochastic nature, the algorithim should be applied repeatedly with different initial points each time to guarantee optimal results (Lavric et al., 2005).

Recently, genetic algorithms have been succesfully implemented in solvers and applied to small problems (Alva-Argàez et al., 2007). Closely related to genetic algorithms is ant colony optimisation which was inspired by the ants' aptitude to find the shortest possible distance between their nests and food supply (Lavric et al., 2005).

The adaptive random search (ARS) method starts by selecting a starting point which can be obtained using a good initialisation technique. Another point is then randomly selected (based on a large/small step size) and a solution evaluated. This solution is then compared with the initial (previous) solution and the decision is made to continue or terminate the procedure (Edgar & Himmelblau, 1988)

Poplewski and Jezowski (2007) applied a simple adaptive random search optimisation technique for the design of an optimal wastewater treatment network. In their solution approach, the authors divided the variables into two; decision variables and independent variables. The decision variables were determined using ARS optimisation while the dependent variables where obtained by sequentially solving a set of linearised equality constraints (Poplewski & Jezowski, 2007).

Generally, stochastic optimisation methods reliably obtain optimal solutions however, they require relatively long CPU times to obtain optimal results and are likely to encounter difficulties when applied to large-scale problems. As such, efforts to improve the method further have been suggested (Jezowski, 2010).

2.6.3.5 Deterministic optimisation

Deterministic optimisation approaches are characterised by the use of convex relations. They take advantage of the mathematical structure or analytical properties of the problem to generate a sequence of points that converge to a global optimum (Lin et al., 2012). The special mathematical structure may be in terms of continuity in the functions or bounds on variables. As highlighted earlier, the nonlinear nature of the water network problem results in convergence difficulties and renders the application of standard NLP techniques ineffective (Galan & Grossmann, 1999; Karuppiah & Grossmann, 2006). As such, the convexification strategies presented earlier are usually combined with deterministic algorithms to guarantee a global optimum (Grossmann & Biegler , 2004; Still & Westerlund, 2010).

The deterministic optimisation technique is gaining popularity in the field because it gives more reliable results as far as global optimality is concerned. As such, most of the recent work in the optimisation of integrated water networks has adopted this approach and great progress has been observed (Karuppiah & Grossmann, 2006). The global optimisation techniques include branch and bound methods as well as cutting plane techniques (Jezowski, 2010).

2.6.3.5.1 *Branch and bound Methods*

Many deterministic optimisation algorithms are based on a branch and bound (BB) framework (Zamora & Grossmann, 1998). The method divides the feasible region [l_i,u_i] of a continuous/discrete variable into two sub-regions, [l_i, β] and [β, u_i]. By taking advantage of the reduced domains, the original underestimator is replaced by stronger ones for each region as illustrated in Figure 2.10. Sub-regions that are proved not to contain the optimal solution are then systematically pruned (fathomed) until the optimal solution is attained. The branching technique, whether standard or spatial, is applied in a recursive manner leading to a hierarchy of subproblems that can be represented in a tree structure.

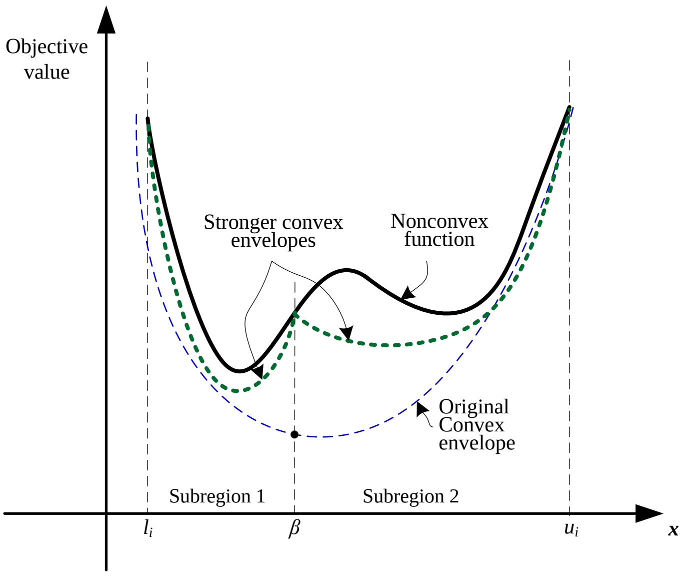


Figure 2.10: Spatial branch and bound technique

Different branch and bound schemes exist and these can be identified depending on how the branching on discrete and continuous variables is performed and also on the tightening of the lower and upper bounds of the variables (Grossmann & Biegler , 2004; Zamora & Grossmann, 1998). Some methods perform the spatial tree enumeration on both discrete and continuous variables. Others branch on the continuous variables and solve the corresponding MINLP problem at each node. Some others branch on the discrete variables and switch to spatial branch and bound at the nodes where feasibility is assured (Grossmann & Biegler , 2004).

An extension to the branch and bound method is the branch and contract technique first introduced by Ryoo and Sahinidis (1996). The technique aims at strategically reducing the variable domain beyond that which can be achieved by branching alone by using range reduction strategies. The range reduction strategies estimate and tighten variable bounds by exposing redundancies, infeasibilities and implied bounds (Zamora & Grossmann, 1998; Karuppiah & Grossmann, 2006). Most of the techniques heavily rely on variable discretisation (Faria & Bagajewics, 2011). A number of these bound tightening strategies have been presented by Tawarmalani and Sahinidis (2004). The technique is usually performed in association with LP relaxations rather than complex convex relaxations since for the former sensitivity information is readily available and easier to interpret than for the latter (Faria & Bagajewics, 2011).

Quesada and Grossmann (1995) proposed a branch and reduce (contract) method for nonconvex NLP problems. By making use of linear and nonlinear underestimators for convexification, the authors managed to apply a branch and contract algorithm on concave separable, linear fractional and bilinear programs. Using a similar technique Zamora and Grossmann (1998) managed to solve a distributed effluent treatment problem. Tawarmalani and Sahinidis (2004) developed a spatial branch and contract method that branches on the continuous and discrete variables and has been successfully implemented in the global solver BARON. Figure 2.11 shows the steps that the BARON algorithm takes during the solution process.

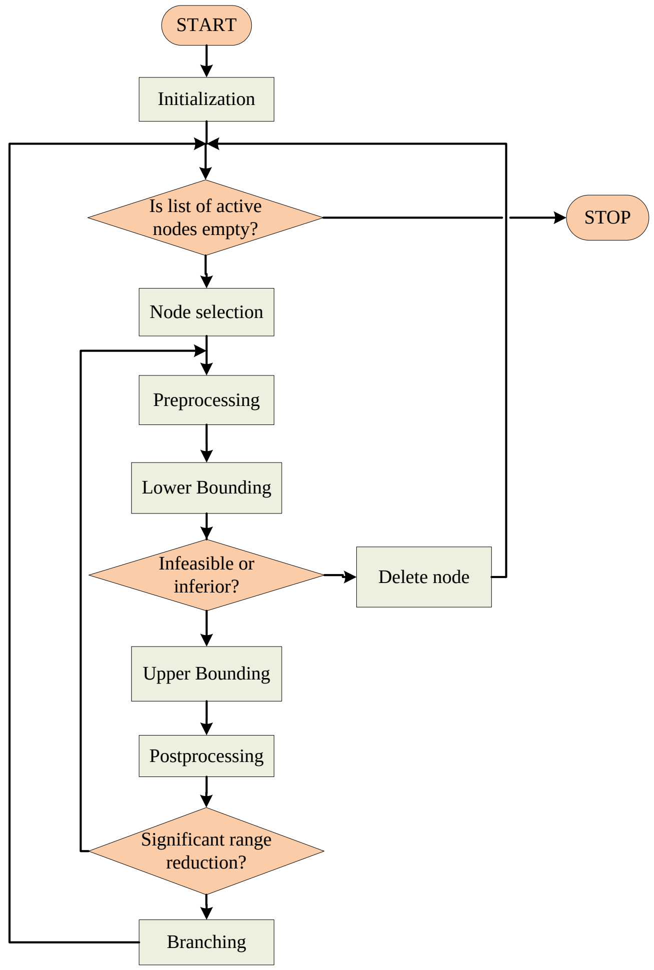


Figure 2.11: BARON algorithm steps.

More recently, Faria and Bagajewics (2011) presented a novel bound contraction procedure that does not require variable discretisation. A significant number of studies on water minimisation solved the optimisation problem through the use of similar combinatorial searches where all the possible water reuse structures are analysed using a tree-type search using a branch and bound strategy (Ahmetovic & Grossmann, 2010; Karuppiah & Grossmann, 2006; Chew et al., 2009; Khor et al., 2011; Ponce-Ortega et al., 2010).

2.6.3.5.2 Cutting plane methods

The method of cutting planes is used to solve optimisation problems with integer variables. They are successive approximation algorithms that depend on generating a polyhedral outer approximation of the feasible set, which is improved successively by adding valid cuts (Duran & Grossmann, 1986). During the iteration, lower and upper bounds of the optimal value are generated that converge towards the optimal value. Cutting plane techniques include extended cutting planes, outer approximation and benders decomposition method (Nowak, 2005). Figure 2.12 illustrates the method of extended cutting planes.

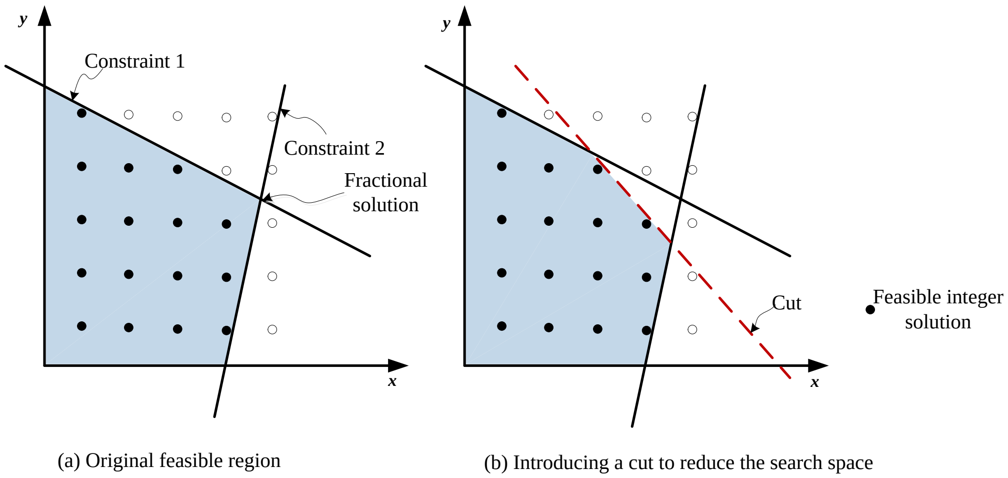


Figure 2.12: The method of extended cutting planes.

The extended cutting planes method works by solving the linear relaxation of the integer problem and the optimum is tested for being an integer solution. If not, there should exist a linear inequality that separates this current non-integer optimum from the convex envelope of the true feasible set thereby making it infeasible to the linear relaxation (Nowak, 2005). This special constraint is a cut and should satisfy the following:

i. every feasible integer solution is feasible for the cut
ii. the current fractional solution is not feasible for the cut

Finding such an inequality is called the separation problem. A cut generated by solving MILP subproblems can be added to the relaxed linear program until the optimal basic feasible solution takes on integer values. This tightens the formulation by removing undesirable fractional solutions without the undesirable side-effect of creating additional sub-problems. This process is repeated until an optimal integer solution is found (Nowak, 2005). The method's main strength is that it heavily relies on the solutions of the MILP problems for which powerful algorithms are readily available however, the method has been criticised because its convergence speed is relatively slow (Westerlund & Petterson , 1995).

In a somewhat similar way, outer approximation makes use of an approximate MILP master problem defined by linearising the nonlinear objective and constraint functions and adding cuts obtained from the solution of the NLP subproblems obtained from fixing the integer variables (Gueddar & Dua, 2012). The solution of the MILP master problem gives a non-decreasing lower bound, while the solution of the NLP subproblem gives an upper bound on the optimal value. The method alternatively solves the MILP master problem and the NLP subproblem until the tolerance gap between the upper and lower bound is met, after which the procedure terminates (Nowak, 2005).

Generalised Benders decomposition (GBD) is similar to the outer approximation method except in the linear master problem. The master problem of the GBD depends on the duality theory and therefore only considers the discrete variables and the active inequalities (Nowak, 2005; Geoffrion, 1972; Duran & Grossmann, 1986). Cuts obtained from the solution of the NLP subproblems formulated by fixing the discrete variables of constraint functions are added (Duran & Grossmann, 1986). According to literature, the lower bound generated by the outer approximation method is greater than or equal to that by the GBD and as such OA always has fewer iterations than GBD (Gueddar & Dua, 2012).

All these cutting methods require that the MINLP problem be convex and as such they are usually combined with effective convexification strategies to form robust algorithms that can be used for MINLP problems (Nowak, 2005). For instances, Porn, et al., (1999) solved an optimisation problem using a novel deterministic global optimisation algorithm which involved solving a sequence of underestimating convex MINLP problems using an extended cutting planes algorithm. Still and Westerlund (2010) developed a sequential cutting plane algorithm that can be used as a sub-solver for MINLP algorithms. To guarantee global optimality the ECP approach required that all inequality constraints be convex and all equality constraints and objectives be linear. As such, they made use of appropriate transformations to convexify all nonconvex parts of the problem (Pörn et al., 1999).

The methods of cutting planes have been successfully embedded within global optimisation solvers and to date they play a significant role in most of the commercial MILP and MINLP solvers used. The algorithms employ mathematical decomposition based generic schemes and these include the α–ECP solver which is based on the extended cutting planes technique and DICOPT (discrete and continuous optimiser) solver which is a direct extension of the OA algorithm. Figure 2.13 shows a simplified solution procedure for the DICOPT algorithm.

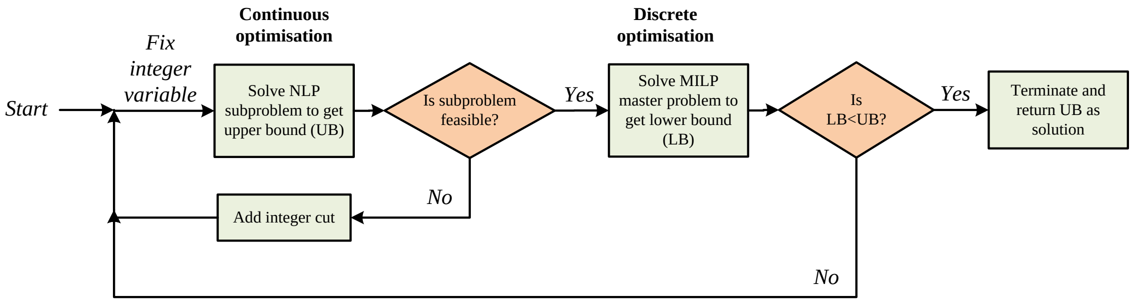


Figure 2.13: Simplified DICOPT algorithm.

Hybrid deterministic approaches between branch and bound methods and cutting planes also exist. These include a hybrid BB and OA approach that updates a BB method for solving the MILP master problem proposed by Zamora and Grossmann (1998). Despite the merits of guaranteeing globally optimum results, deterministic approaches tend to be computationally expensive. Literature has shown that a lot of the combinatorial problems which the deterministic methods try to solve belong to a group of inherently intractable problems commonly referred to as NP-hard. These problems are essentially difficult to solve (Nowak, 2005).

2.7 Hybrid Models

Hybrid models are models that merge physical insights from water pinch with powerful mathematical programming tools in order to produce optimum results. They are essentially optimisation targeting techniques that involve the development of targeted models at a conceptual stage. Early works that presented the idea of hybrid models were predominantly mathematical while later methods incorporated concepts of insight-based methods into the mathematical programming platform to determine minimum flowrates or cost targets for the resource conservation network developed (Tan et al., 2009).

2.7.1 Early Attemps

The work of Dhole et al. (1996) was amongst the first to present the idea of using hybrid models for water network optimisation. As mentioned earlier their work was aimed at overcoming the limitations of using the early mass-transfer based water pinch technique which was incapable of handling water gain/loss as well as multiple aqueous feed streams. As such, by means of mathematical programming using a fixed-flowrate framework, they determined the network design and then developed a graphical representation somewhat similar to that for water pinch.

In the method, each operation is considered to have aqueous inlet and outlet streams and all input requirements (sinks) are plotted together to form the demand composite while the water sources are also plotted together to form the source composite. The axes for these graphical representations are concentration and flowrate and both sources and sinks are assumed to have fixed concentrations. As such, the plots are made up of horizontal and vertical lines. The two composites are plotted together on the same axes and shifted so that they just touch. Figure 2.14(a) shows typical composite curves (also called purity profiles) for the new technique.

Overlaps between the two curves show opportunity for water reuse and is limited by a pinch which can be eliminated by the mixing of source streams as depicted in Figure 2.14(b). Targets for minimum freshwater intake and wastewater generation are also set in this method. Reviewers highlighted that the technique has a limitation in that it has no systematic method for the elimination of pinch points via mixing and therefore present mixing uncertainties.

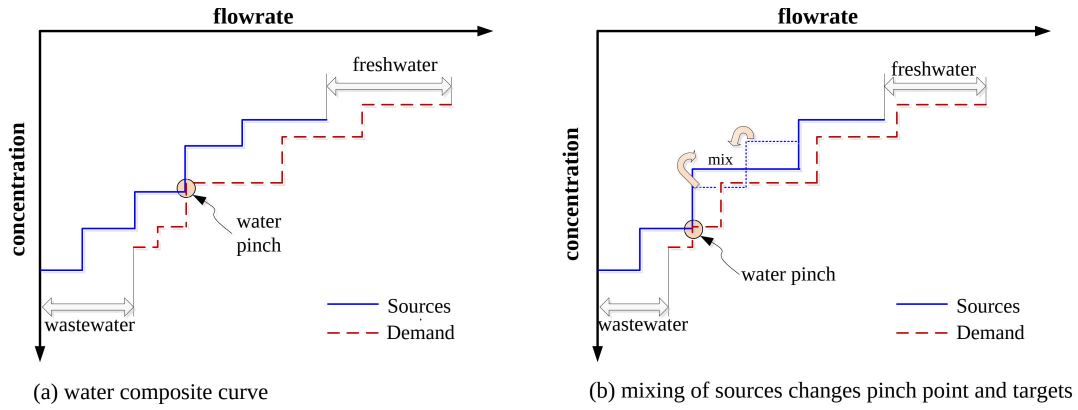


Figure 2.14: Graphical representation of method by Dhole et al. (1996).

El-Halwagi et al. (2003) developed a new non-iterative, systematic, and graphical targeting technique building on from the work of Dhole et al. (1996) and the ideas presented by Hallale (2002). First, the problem is formulated mathematically to provide a systematic basis for its solution and then optimality conditions are derived using dynamic programming formulation and parametric optimisation. From there, these conditions are converted into a graphical representation that can be readily used to identify rigorous targets for minimum usage of fresh resources. The method proved useful for providing physical insights into the use of freshwater and the interactions between sources and sinks.

Doyle and Smith (1997) made a significant contribution to the use of hybrid models to tackle water network problems. According to Doyle and Smith, (1997), using the concept of limiting water profiles (all outlet concentrations fixed to their maximum for sinks and to zero for the treatment units) to describe all the water-using operations allows for the analysis of complete water networks on a common basis. The authors developed a method for water minimisation through reuse, that made use of a hybrid of mathematical programming and water pinch which incorporated all constraints (Doyle & Smith, 1997).

By means of an iterative optimisation procedure that uses a linear programming (LP) approximation as a starting point the authors managed to solve the NLP problem. The solution was then used to develop a graphical representation that provided insights into the problem. The technique had the advantage of being able to deal with large complex sets of problems that previous water pinch was in capable of doing (Doyle & Smith, 1997).

2.7.2 Automated Designs

The methods by Dhole (1996) and Doyle and Smith (1997) are inherently mathematical considering that the targeting and design were achieved using mathematical techniques. The graphical representations were developed in accordance with the results obtained using mathematical programming. Having realised this gap, Alva-Argaez et al. (1998) proposed a hybridt approach that systematically integrated water pinch analysis within an optimisation framework. Water pinch based targeting heuristics which support a decomposition-based solution procedure were incorporated into the network. The problem formulated as an MINLP was decomposed into a sequence of MILP problems which were solved using a branch and bound algorithm to approximate the optimal solution. The authors called the method the 'automated design' technique.

It was the seminal work of Alva-Argàez (1998) that inspired a new breed of hybrid models in the field. Gunaratnam et al., (2005) proposed an automated design method for the design of industrial water systems with reuse, regeneration reuse and regeneration recycle. Water using operations were described by limiting water profiles and the grouping strategy from water pinch was applied in the optimisation framework to prevent closed paths in the final design. The concept of limiting water profiles they adopted ensures linear formulations and hence convexity. The MINLP problem was decomposed into MILP and LP problems (linearisation of the function describing the cost of operating treatment units) for initialisation and then the design fine-tuned using an MINLP algorithm.

In a later work, Alva-Argàez (2007) proposed a new decomposition approach to extend their work on water network synthesis for refineries. Like the previous methods, this approach made use of conceptual insights to define successive projections in the solution space. As literature highlights, the automated design approach does not guarantee a global optimum and therefore is viewed as a decision support tool to eliminate alternatives (Gunaratnam et al., 2005; Khor et al., 2014).

2.8 Wastewater Regeneration

For a long time water treatment focused on the use of end-of-pipe wastewater treatment as the sole remedy to meet effluent discharge limits (Bagajewicz & Savelski, 2000). This concept works well with the conventional physical, chemical, thermal and biological treatment methods as these require a lot of space and are at some instances carried out off-site. Over the years the scarcity of water, rising energy costs, and stricter environmental legislation has created a new and different view on water consumption and wastewater treatment. Focus has shifted towards solutions that maximise water reuse/recycle. Water regeneration is one of the solutions.

The efficient treatment of wastewater to meet required quality standards is a critical element for wastewater reuse and the changes required to make the wastewater reusable have become the basis for water regeneration (Sharma & Sanghi, 2013). Water quality required for recycle and reuse is different from water quality acceptable for discharge, the two of which are dictated by process requirements and environmental regulations. As such, where recycle/reuse exists the regeneration units have to be carefully intertwined such that both standards are met without incurring unnecessary costs, hence the need for optimisation.

2.8.1 Black-box Regeneration

Water regeneraton within water networks has been considered in a number of published papers. In most instances either the regenerator technology and performance, number of regeneration units and arrangement of the regeneration train or regeneration design parameters are not set as decision variables. Rather they are assumed to be known and fixed or represented in oversimplified ways (Rangaiah & Wei, 2010). Khor et al. (2011) referred to this ideology as the ‘black-box’ concept. According to Galan and Grossmann (1998), although some conventional treatment technologies (biological, chemical and physical) can be approximated in this way, others like membrane technologies do not follow a similar approximation.

Few studies have considered the development of stand-alone detailed regenerator models for water networks. The more recent works have increasingly involved rigorous optimisation-based models, particularly for membrane-based technologies (Khor et al., 2014). Reverse osmosis models have been developed by El-Halwagi (1992) and Saif et al. (2013). Work on electrodialysis has been presented by Lee et al. (2002), Tsiakis and Papageorgiou (1995) and Strathmann (2010). Zeman and Zydney (1996) and Brunah et al. (2006) addressed work on ultrafiltration and microfiltration.

Different treatment technologies have different advantages and disadvantages over others and as such the treatment technologies of choice that match the system under consideration have to be identified. Numerous researchers have failed to identify the type used, while others give umbrella terms, such as ‘membrane based’, ‘non-membrane-based’ or ‘biological’, to identify the type without specifying the actual technology adopted.

For regenerator performance, the norm has been to represent it by means of fixed removal ratios or fixed exit concentrations with energy consumption terms embedded implicitly within simplified linear cost functions. For instance, in the study by Galan and Grossmann (1998), in one example they considered regenerator technology selection and the options they had for treatment were physical, biological and chemical treatment. The performances of these units were described in a black-box fashion. Many more studies that adopt the same black-box idea have been presented by other authors as shown in Table 2.1.

In another example, Galan and Grossmann (1998) considered non-dispersive solvent extraction as the treatment technology and they used shortcut models in a ‘grey-box’ fashion to represent the unit performance. Grey-box in this context describes an intermediary model between a black-box and a detailed model (white-box). Similarly, Alva-Argaez et al. (1998) addressed the water network problem and considered the use of steam strippers, API separators, dissolved air floatation units and biological treatment units to meet the environmental requirements, all of which had their performance described by fixed removal ratios.

Table 2.1: Summary of studies on wastewater regeneration network synthesis.

Reference	Reg. technology identity	Reg. config	No. of reg.	Reg. model	Removal ratio
Takama et al. (1980)	foul water stripper, oil separator, coagulating sedimentating & filtration units	distributed	multiple	blackbox	fixed
Alva-Argaez et al.(1998)	steam stripper, dissolved air floatation, API seperator, biological, hydrocyclone	distributed	multiple	blackbox	fixed
Zamora & Grossmann (1998)	unidentied	distributed	multiple	blackbox	fixed
Galan & Grossmann (1998)	physical, biological chemical	distributed	multiple	blackbox	fixed
Galan & Grossmann (1999)	nondispernsive solvent extraction	distributed	multiple	shortcut	fixed
Huang et al.(1999)	steam stripper, API separator	centralised	multiple	blackbox	fixed
Gunaratnam et al. (2005)	unidentified nondispernsive solvent extraction	distributed	multiple	bleckbox & shortcut	fixed
Chang & Li (2005)	unidentified	distributed	multiple	blackbox	fixed
Meyer & Floudas (2005)	unidentified	distributed	multiple	blackbox	fixed
Karuppiah & Grossmann (2006)	unidentifeid	distributed	multiple	blackbox	fixed
Tan et al. (2009)	partitioning regenerator	distributed	single	blackbox	fixed
Ahmetovic & Grossmann (2010)&(2011)	unidentified	distributed	multiple	blackbox	fixed
Khor et al. (2011)	reverse osmosis	distributed	single	detailed	fixed
Khor et al. (2012)	mud trap, dissolved air floatation, multimedia filter, ultrafiltration, reverse osmosis	distributed	multiple	blackbox	fixed
Yang et al.(2014)	reverse osmosis, ion exchange, ultrafiltration, activated sludge and trickle filters	distriduted	multiple	shortcut	variable

More recently, Yang et al. (2014), made use of short-cut models of the regenerators having identified the technology types available. They considered using reverse osmosis, ion exchange, ultrafiltration, activated sludge and trickle filters for wastewater regeneration.

Closely related to the performance of the treatment units are the design parameters for the units. These includes the length of the unit, number of membrane modules/cell pairs, pressure drop and membrane area. It is these design parameters that determine the units' performances as well as the capital and operating costs associated with the units. The design variables can be determined by the use of detailed or shortcut models as shown by El-Halwagi (1992), Tsiakis and Papageorgiou (1995), Galan and Grossmann (1999), Khor et al. (2011) and Yang et al. (2014). The black-box concept ignores the design of the regeneration network.

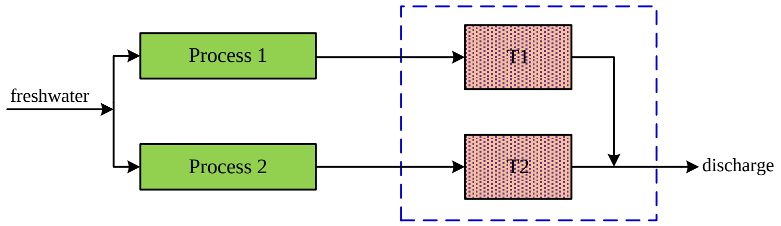
The arrangement of the regeneration train concerns the topology and synthesis of the regeneration network. It includes the way in which the different regeneration units are connected together to achieve the target concentrations and water recoveries. Synthesis of the network is related to the design depending on the system and the limitations of the treatment technology at hand. For instance, it may be possible for a single regenerator, operating at its maximum capacity, to be incapable of achieving contaminant removal targets that two/three regenerators would be able to achieve. In this instance, the assumption of using one treatment unit may lead to unrealistic and erroneous results, hence simultaneous design and topological considerations within the regeneration network have to be made.

Chang and Li (2005) confirm the merits in the philosophy of using multiple regenerators. However, the authors also highlight the need for the system to choose only the necessary treatment units even if it means by-passing other available units. Most researchers that have considered the use of multiple regenerators have also taken this into account for the synthesis of optimal regeneration networks. This includes El-Halwagi (1992), Alva-Argaez et al. (1998), Galan and Grossmann (1998), Khor et al. (2012) and Yang et al. (2014).

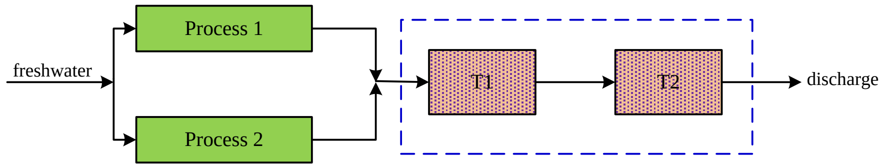
2.8.2 Distributed Water Treatment

As highlighted earlier, in the process industry, the conventional water treatment practices have been to operate a common sequential centralised end-of-pipe wastewater treatment plant. In this scheme all wastewater streams are merged into one before being fed into series of physical, biological and chemical treatment operations (Wang &

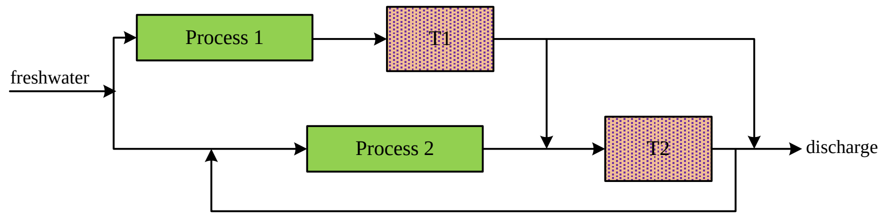
Smith, 1994b; Galan & Grossmann, 1998; Chew et al., 2009; Tan et al., 2009). Recent efforts have shifted towards distributing and decentralising the treatment operations motivated by the fact that the cost of treatment is largely attributed to the quantity of wastewater treated. Figure 2.15 illustrates the differences between centralised and decentralised treatment operations.



(a) Distributed centralized treatment system



(b) Sequential centralized treatment system



(c) Distributed decentralized treatment system

Figure 2.15: Difference between centralised and decentralised treatment networks.

In distributed treatment schemes, streams are either treated separately or only partially mixed thereby reducing flowrates into the treatment unit and reducing the capital and operational costs (Wang & Smith, 1994b; Galan & Grossmann, 1998; Karuppiah & Grossmann, 2006). This suggests that wastewater streams should be segregated from effluent treatment and only combined if appropriate.

In the context of water minimisation, Wang and Smith (1994b) and Kuo and Smith (1997) were among the first to consider the design of distributed water treatment systems. By means of water pinch analysis they determined the final design of the final waste disposal network from networks of alternative designs. The approach of Wang and Smith (1994b) did not incorporate important design features of the distributed effluent treatment systems and in light of these shortcomings, Kuo and Smith (1997) extended the method by employing a detailed design evaluation strategy and by extending the concepts to retrofit cases (Kuo & Smith, 1997).

Galan and Grossmann (1998) were the first to introduce a superstructure based optimisation approach for the simultaneous synthesis and design of optimal distributed effluent treatment systems. Their superstructure was based on the work by Wang and Smith (1994b). The authors only focused on the regeneration network and they considered the use of a distributed effluent treatment system. The results of their work proved that when flexibility is allowed for the treatment units to be distributed and only combined at the optimiser's discretion, better solutions for the water network are guaranteed.

Alva-Argaez (1998) and Gunaratnam et al. (2005), by adopting a hybrid technique, tackled the water-regeneration network problem. A significant observation that they made was that a decentralised water system allows for multiple regenerator technologies to be incorporated into the network and through optimisation, the best available technology for treatment of the different wastewater stream can be determined. Zamora and Grossmann (1998) also addressed the wastewater regeneration network synthesis problem first presented by Kuo and Smith (1997) using a global optimisation algorithm. For both cases, the optimum results favoured a distributed effluent treatment system.

2.8.3 Best Available Technology

The selection of the regeneration technology to adopt in a water network is dependent upon many factors, most of which are dependent on the operations taking place in the plant and on the mechanism of regeneration. This is where property integration comes into play, where the allocation and manipulation of streams and units is based on tracking, adjustment, assignment and matching of functionalities occur. In this way it is possible for two different technologies to remove contaminants at different investment and operating costs thus the need to optimise the technology selection becomes apparent (Galan & Grossmann, 1998).

Literature shows that, for a water network with multiple treatment unit capabilities, arbitrarily deciding the method of treatment can lead to topological traps that lead to higher costs being incurred. Alva-Argaez et al. (1998) in their work proved that issues concerning the best available technology are far from trivial and that simultaneous optimisation of the entire system is imperative to ensure the appropriate choice of technology for water treatment.

Quite a number of studies have considered the use of multiple technologies for water treatment. In water pinch, Tan et al. (2007) considered the use of dissolved air floatation tanks and saveall disc filters as regenerator technologies for wastewater purification. As for mathematical programming, authors include Alva-Argaez et al. (1998) and Gunaratnam et al. (2005) who considered using steam strippers, API separators, dissolved air floatation units, hydrocyclones and biological treatment units. Galan and Grossmann (1999) used short-cut models for non-dispersive solvent extraction which were differentiated by delegating different removal ratios to the different units hence the concept of multiple technologies, for the synthesis of optimal water networks. Refer to Table 2.1 for information on other authors.

From these cases, an interesting observation is that, for most regenerators considered in the networks, the regenerator performances are fixed. Literature has shown that, in the real world, plant operations are not as straightforward (Tan et al., 2009). For instance, it is possible to have two regenerators of the same technology performing differently perhaps on account of the size or age of the equipment (Tsiakis & Papageorgiou, 1995). How then do we know if the performance we have arbitrarily chosen for the treatment unit under assessment is the best given the process conditions at hand? There is no better way of knowing except through optimising the performance as well. Although the performance may be bound by limits adopted from the physical inspection of the real world, of that small range of options to choose from, the best performance for the situation at hand can be determined. Here again the concept of property integration plays a huge role.

At first glimpse, intuition may suggest using regenerators with the highest removal capacity; however, this is not the case as there are trade-offs that need to be made. High regenerator performances imply high water recoveries and contaminant removals but at the expense of high capital and operating cost. Yang et al. (2014) tested the philosophy by making the removal ratios of the different technologies available variable, at the discretion of the optimiser. Although the results of their work had removal ratio upper limits reached (or nearly reached), Yang et al. (2014) confirm that it was due to the holistic properties and demands of the system hence implying that it would not always be the case for a different system. As such, it suffices to state that simultaneous optimisation of the regenerator technology selection and the regenerator performance guarantees better results in terms of costs, as compared to having them arbitrarily fixed.

2.8.4 Membrane technology

According to Sharma and Sanghi, (2013), the treatment requirements for industrial wastewater are dependent upon the origin of the water and the application for which it will be used. Conventional methods for water reclamation included clarification, distillation and adsorption (Judd & Jefferson, 2003). Literature has shown that membrane technology is gaining popularity over these conventional methods mainly because:

i. membranes have high selective separation
ii. they allow for continuous, automatic and economical separation at room temperature
iii. their compactibility allows for simple integration into already existing plant processes
iv. they do not require chemical addition to enhance the process
v. membranes are characterised with appreciable energy savings (Judd & Jefferson, 2003)

Membranes are materials that allow for the selective passage of certain species based on their physical or chemical properties. Species that are allowed to pass through are usually referred to as the permeate and those that are not allowed are usually called the reject or retentate. The degree of selectivity of a membrane is dependent on the physical (e.g. pore size) and chemical properties of the membrane as well as the physical and chemical properties of the liquid being handled (Judd, 2006). Figure 2.16 shows a schematic of a basic separation operation by a membrane.

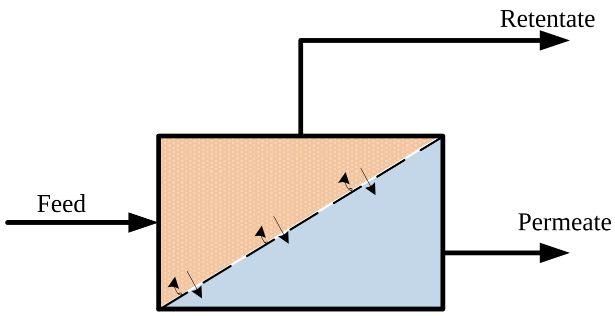


Figure 2.16: Typical membrane separation process.

There exist quite a number of membrane processes and these are categorised based on the driving force that causes the flow of permeate through the membrane. This includes classes such as pressure-driven processes, potential difference driven processes, temperature- driven processes and concentration-driven processes. Table 2.2 gives a summary of the categories available and the respective examples within each category.

According to Judd (2006), mature membrane technology applications for water and wastewater treatment are limited to pressure driven operations and electrodialysis. Extensive work on the use of pressure-driven membranes within water networks has been carried out and very little work has considered electrodialysis. As such, the current study focuses on the use of electrodialysis technology for wastewater regeneration.

Table 2.2: Classification of membrane processes (Wang et al., 2011).

Driving force	**Principle of operation**	**Examples**
Pressure-driven	Hydraulic pressure is applied to speed up the separation of species based on the species' size	Reverse osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF), Microfiltration (MF), Pervaporation (PV), Membrane gas separation
Temperature-driven	Separation is induced by a vapour pressure gradient that arises from a temperature difference across the membrane	Membrane distillation (MD)
Electrical potential-driven	Electrical potential is applied to facilitate the separations of charged and uncharged species	Electrodialysis (ED) Bipolar membranes
Concentration-driven	Separation achieved by virtue of the species' different diffusion rates	Dialysis Membrane extraction

2.9 Electrodialysis

2.9.1 Background

Electrodialysis has been used for the desalination of brackish water to obtain portable water for over 50 years now. The process has been extended and modified for applications in the food industry as well as in the process industry where it can be used for wastewater treatment (Strathmann, 2010). According to literature, nanofiltration has overtaken electrodialysis in terms of efficiency as far as the desalination of brackish water is concerned. As such, the focus on applications of electrodialysis has shifted from desalination to wastewater treatment in the process industry. Electrodialysis in conjunction with other related processes such as reverse electrodialysis and ion-exchange resins have become of great relevance in the production of high quality industrial water and are considered state of the art technology. Interest in the technology continues to grow as other applications for it continue to be identified (Strathmann, 2010).

2.9.2 Operating Principle

In principle, the process is based on the electro-migration and selective transport of ionic species induced by an electric current through a series of alternately arranged anion and cation-exchange membranes (EPRI, 1997; Strathmann, 2010). Figure 2.17 is a schematic of a typical electrodialysis cell arrangement that can be used to illustrate the operating principles of the process.

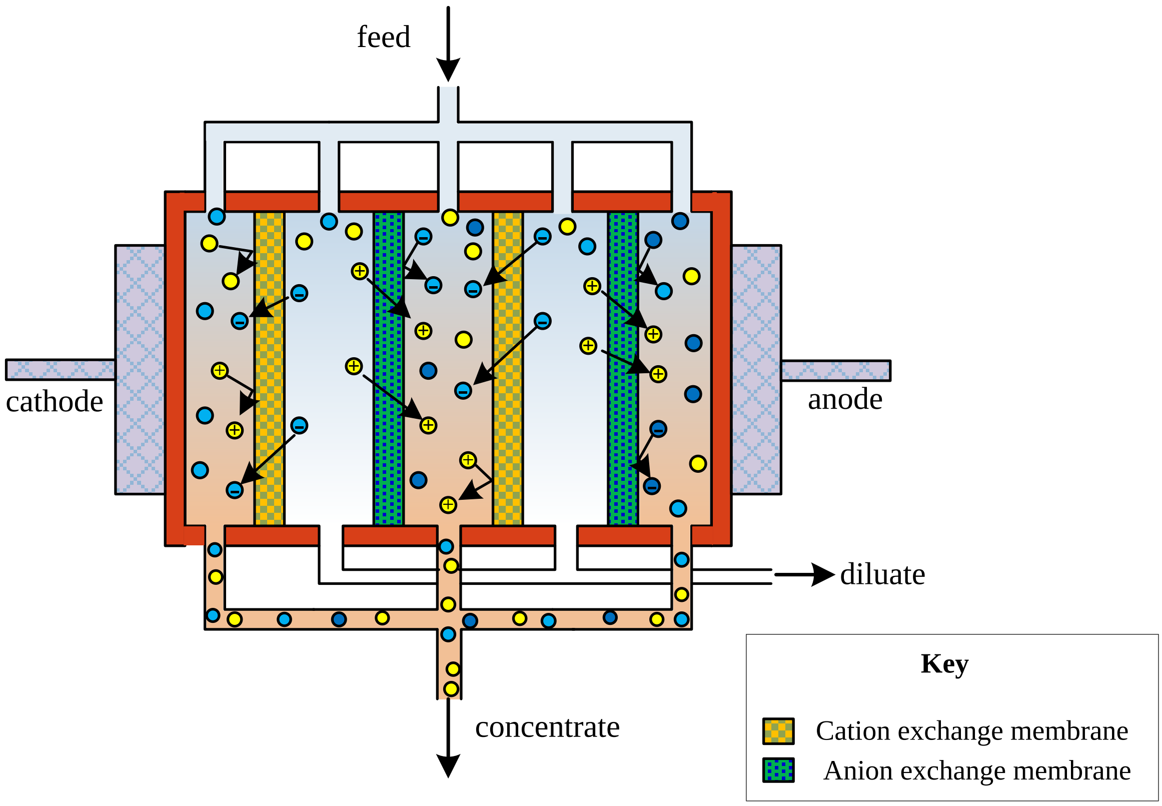


Figure 2.17: Typical Electrodialysis cell arrangement.

When in operation, direct current is applied on the electrodes and as a result cations migrate towards the cathode whilst anions migrate towards the anode (Costa et al., 2002). Movement of the ions is controlled by the ion-exchange membranes which only allow either the cations if it is a cation-exchange membrane or the anions if it is an anion-exchange membrane to pass through (Strathmann, 2010; Tsiakis & Papageorgiou, 2005). As such, alternate channels of diluate (permeate) streams and concentrate (reject) streams are formed as shown in Figure 2.17. A diluate stream, a concentrate stream together with the cation and anion-exchange membranes make up a repeating unit called a cell pair. A single electrodialysis entity often referred to as a stack may contain several hundreds of cell pairs (Tsiakis & Papageorgiou, 2005; Strathmann, 2010).

2.9.3 Design

Based on the operating principle of electrodialysis, the important variables that help in the decision making process for the selection and design of the system can be easily identified. These include electric current, membrane area, stack length, pumping energy requirements and pressure drop across the unit. The accurate determination of these design variables requires technological insight, adequate and accurate mathematical relations to allow for process simulation and appropriate optimisation tools to be applied. Tsiakis and Papageorgiou (2005) studied the design of an optimal electrodialysis plant and in their work they consolidated important mathematical relations from previous research and developed a model for the process. Their focus was on the minimisation of costs and their objective function composed of both capital costs and operational costs of the plant (Tsiakis & Papageorgiou, 2005).

Most of the mathematical formulations presented by Tsiakis and Papageorgiou (2005) were obtained from Lee et al. (2002), who addressed the derivation of the relations in detail. By applying basic geometry, relevant assumptions and mathematical manipulations, Lee et al. (2002) managed to derive relations for membrane area, stack length, diluate flowrate, pressure drop and pumping energy. The formulation for the electric current required was obtained from electrochemistry insight while the electric density was determined empirically (Lee et al., 2002; Tsiakis & Papageorgiou, 2005). As such, the capital cost which is comprised of the membrane area cost and piping costs as well as the operating costs comprising of the energy costs, freshwater cost and wastewater treatment cost were determined fairly accurately.

2.9.4 Limitations

According to Strathmann (2010), all electro-membrane processes and components adapted for this particular process still have inherent limitations and even with the substantial on-going development there still exist gaps that need to be filled to improve the process. For instance, electrodialysis works best with low molecular weight ionic components while uncharged and less mobile species of high molecular weight are not significantly removed. The latter case can be encountered for feed sources that contain a lot of suspended solids or microorganisms and for such a situation a pre-treatment step has to be considered prior to electrodialysis processing.

2.10 Conclusion

From this comprehensive review on the optimisation of water networks, it is clear that there still exist gaps in determining accurate representations of water networks. As such, the current work considers the use of detailed models of electrodialysis regenerators to capture the design features of the units such that optimal synthesis and design are simultaneously attained. Faria and Bagajewicz (2011) confirm that the only way to advance in the field when detailed models are used, is to use mathematical programming and hence in the current work optimisation is carried out using mathematical programming.

2.11 References

Ahmetovic, E. & Grossmann, I. E., 2010.Strategies for the Global Optimisation of Integrated Process Water Networks. *20th European Symposium on Computer Aided Process Engineering,* Volume 20, pp. 901-906.

Ahmetovic, E. & Grossmann, I. E., 2011. Global superstructure optimisation for the design of integrated process water networks. *AIChE Journal,* 57(2), pp. 434-457.

Alva-Argaez, A., Kokossis, A. C. & Smith, R., 1998. Wastewater Minimisation of Industrial Systems using an Integrated Approach. *Computers and Chemical Engineering,* Volume 22, pp. S741-S744.

Alva-Argàez, A., Kokossis, A. C. & Smith, R., 2007. The Design of water-using systems in petroleum refining using a water-pinch decomposition. *Chemical Engineering Journal*, Volume 128, pp. 33-46.

Bagajewicz, J. M. & Savelski, M. J., 2000. On the optimality conditions of water utilisation systems in process plant with single contaminats. *Chemical Engineering Science,* 55(21), pp. 5035-5048.

Bagajewicz, M., 2000. A review of recent design procedures for water networks in refineries and process plants. *Computers and Chemical Engineering,* Volume 24, pp. 2093-2113.

Bagajewicz, M. J., Rivas, M. & Savelski, M. J., 2000. A robust method to obtain optimal and sub-optimal design and retrofit solutions of water utilisation systems with multiple contaminants in process plants. *Computers and Chemical Engineering,* Volume 24, pp. 1461-1466.

Bagajewicz, M. & Savelski, M., 2001. On the use of Linear Models for the Design of Water Utilisation Systems in Process Plants with a Single Contaminant. *Institution of Chemical Engineers,* Volume 79, pp. 600-610.

Bandyopadhyay, S. & Cormos, C.-C., 2008. Water Management in Process Industries Regeneration and Recycle through a Single Treatment Unit. *Industrial & Engineering Chemistry Research,* Volume 47, pp. 1111-1119.

Bartels, W., 2012. *Water Scarcity: A dive into global reporting trends,* s.l.: KPMG International Cooperative.

Brunah, G. L., Venkiteshwaran, A. & Belfort, G., 2006. Global Model for Optimising Crossflow Microfiltration and Ultrafiltration Processes: A New Predictive and Design Tool. *Biotechnology Progress,* Volume 21, pp. 1013-1025.

CanmetENERGY, 2003. *Pinch Analysis for the Efficient Use of Energy, Water and Hydrogen*. [Online] CanmetENERGY Available at: https://www.nrcan.gc.ca [Accessed 20 July 2015].

Chang, C.-T. & Li, B.-H., 2005. Improved Optimisation Strategies forGenerating Practical Water-Usage and Treatment Network Structures. *Industrial and Engineering Chemistry Research,* Volume 44, pp. 3607-3618.

Chew, I. M. L., Tan, R. R., Foo, D. C. Y. & Chiu, A. S. F., 2009. Game theory approach to the analysis of inter-plant water integration in an eco-industrial park. *Journal of Cleaner Production,* Volume 17, pp. 1611-1619.

Costa, R. F. D., Klein, C. W., Bernardes, A. M. & Ferreira, J. Z., 2002. Evaluation of the Electrodialysis Process for the Treatment of Metal Finishing Wastewater. *Journal of the Brazilian Chemical Society,* 13(4), pp. 540-547.

Dhole, V. R., Ramchandi, N., Taish, R. A. & Wasikewski, M., 1996. Make your process water pay for itself. *Chemical Engineering,* 103(1), pp. 100-103.

Doyle, S. J. & Smith, R., 1997. Targeting water reuse with multiple contaminants. *Institute of Chemical Engineers,* Volume 75, pp. 181-189.

Duran, M. A. & Grossmann, I. E., 1986. An Outer-Approximation Algorithm for a Class of Mixed-Integer Nonlinear Programs. *Mathematical Programming,* Volume 36, pp. 307-339.

Edgar, T. F. & Himmelblau, D. M., 1988. *Optimisation of Chemical Processes.* New York: McGraw-Hill.

El-Halwagi , M. M. & Manousiouthakis, V., 1989. Synthesis of mass exchange networks. *AIChE Journal,* 35(8), p. 1233–1244.

El-Halwagi, M. M., 1992. Synthesis of Reverse-Osmosis Networks for Waste Reduction. *American Institute of Chemical Engineers,* 38(8), pp. 1185-1198.

El-Halwagi, M. M., 2012. *Sustainable Design Through Process Integration: Introduction to Sustainability, Sustainable Design, and Process Intergration.* Waltham, MA: Elsevier Inc..

El-Halwagi, M. M., Gabriel, F. & Harell, D., 2003. Rigorous Graphical Targeting for Resource Conservation via Material Recycle/Reuse Networks. *Industrial Engineering and Chemistry Research,* Volume 42, pp. 4319-4328.

El-Halwagi, M. M., Hamad, A. A. & Garrison, G. W., 1996. Synthesis of waste interception and allocation networks. *AIChE Journal,* 42(11), p. 3087–3101.

EPRI, 1997. *Membrane Technologies for Water and Wastewater Treatment,* California: Electric Power Research Institute (EPRI).

Faria, D. C. & Bagajewics, M. J., 2011. Novel bound contraction procedure for global optimisation of bilinear MINLP problems with applications to water management problems. *Computers and Chemical Engineering,* Volume 35, pp. 446-455.

Galan, B. & Grossmann, I., 1998. Optimal Design of Distributed Wastewater Treatment Networks. *Industrial & Engineering Chemistry Research,* Volume 37, pp. 4036-4048.

Galan, B. & Grossmann, I. E., 1999. Optimisation Strategies for the Design and Synthesi of Distributed Wastewater. *Computers and Chemical Engineering,* pp. S161-S164.

Geoffrion, A. M., 1972. Generalised Benders Decomposition. *Journal of Optimisation Theory and Applications*, 10(4), pp. 237-261.

Glover, F., 1975. Improved Linear Integer Programming Formulations of Nonlinear Integer Problem. *Management Science,* 22(4), pp. 455-460.

Grossmann, I. E. & Biegler , L., 2004. Pa II. Future perspective on optmisation. *Computers and Chemical Engineering,* Volume 28, pp. 1193-1218.

Guanaratnam, M. et al., 2005. Automated Design of Total Water Systems. *Industrial and Engineering Chemistry Research,* Volume 44, pp. 588-599.

Gueddar, T. & Dua, V., 2012. Approximate Multi-Parametric Programming based B & B Algorithm for MNILPs. *Computers and Chemical Engineering,* Volume 42, pp. 288 - 297.

Gunaratnam, M. et al., 2005. Automated Design of Total Water Systems. *Industrial and Engineering Chemistry Research,* Volume 44, pp. 588-599.

Gupta, A. & Manousiouthakis, V., 1994. Waste reduction through multicomponent mass exchange network synthesis. *Computers and Chemical Engineering,* Volume 18, pp. S585-S590.

Hallale, N., 2002. A new graphical targetting metod for water minimisation. *Advances in Environmental Research,* Volume 6, pp. 377-390.

Huang, C.-H., Chang, C.-T., Ling, H.-C. & Chang, C.-C., 1999. A Mathematical Programming Model for Water Usage and Treatment Network Design. *Industrial And Engineering Chemistry Research,* Volume 38, pp. 2666-2679.

Jezowski, J., 2010. Review of Water Network Design Methods with Literaure Annotations. *Industrial & Engineering Chemistry Research,* Volume 49, pp. 4475-4516.

Judd, S., 2006. *The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment.* Oxford, UK: Elsevier Ltd..

Judd, S. & Jefferson, B., 2003. *Membranes for Industrial Wastewater Recovery and Re-use.* Oxford, UK: Elsevier Ltd..

Karuppiah, R. & Grossmann, I. E., 2006. Global optimisation for the synthesis of integrated water systems in chemical processes. *Computers and Chemical Engineering,* Volume 30, pp. 650-673.

Khor, C. S., Chachuat, B. & Shah, N., 2012. A superstructure optimisation approach for water network sysnthesis with membrane seperation-based regenerators. *Computers and Chemical Engineering,* Volume 42, pp. 48-63.

Khor, C. S., Chachuat, B. & Shah, N., 2014. Optimisation of Water Network Synthsis for Single-Site and Continuous Procesesses: Milestones, Challenges and Future Direction. *Industrial & Engineering Chemistry Research,* Volume 53, pp. 10257-10275.

Khor, C. S., Foo, D. C., El-Halwagi, M. M. & Tan R. R., Shah N., 2011. A Superstructure Optimisation Approach for Membrane Separation-Based Water Regeneration Network Synthesis with Detailed Nonlinear Mechanistic Reverse Osmosi Model. *American Chemical Society,* Issue 50, pp. 13444-13456.

Koppol, A. P., Bagajewicz, M. J., Dericks, B. & Savelski, M. J., 2003. On the zero water discharge solutions in the process industry. *Advances in Environmental Research,* 8(2), pp. 151-171.

Kuo, W. C. J. & Smith, R., 1998. Design of water-using systems involving regeneration. *Transactions of the Institute of Chemical Engineers, Part B,* Volume 76, pp. 94-114.

Kuo, W.-C. J. & Smith, R., 1997. Effluent treatment system design. *Chemical Engineering Science,* 52(23), pp. 4273-4290.

Lavric, V., Iancu, P. & Plesu, V., 2005. Genetic algorithm optimisation of water consumoption and wastewater network topology. *Journal of Cleaner Production,* Volume 13, pp. 1405-1415.

Lavric, V., Iancu, P. & Plesu, V., 2005. Genetic algorithm optimisation of water consumption and wastewater network topology. *Journal of Cleaner Production,* Volume 13, pp. 1405-1415.

Lee, H.-J., Safert, F., Strahmann, H. & Moon, S. H., 2002. Designing of an electrodialysis desalination plant. *Desalination,* Volume 142, pp. 267-286.

Li, B.-H. & Chang, C.-T., 2007. A Simple and Efficient Initialisation Strategy for Optiming Water-Using Network Designs. *Industrial and Engineering Chemistry Research,* Volume 46, pp. 8781-8786.

Lin, M. H., Tsai, J.-F. & Yu, C.-S., 2012. A Review of Deterministic Optimisation Methods in Engineering and Management. *Mathematical Problems in Engineering,* p. 15 pages.

Lundell, A., 2009. *PHD Thesis: Transformation Techniques for Signomial Functions in Global Optimisation,* Turku, Finland

Lundell, A. & Westerlund, T., 2008. *Exponential and power transformations for convexifying signomial terms in MINLP problems.* CA, USA, ACTA Press Anaheim, pp. 154-159.

Lundell, A. & Westerlund, T., 2012. *Finding an optimised set of transformations for convexifying noncovex MINLP problems.* Turku, Elsevier B. V.

Manan, Z. A., Tan, Y. L. & Foo, D. C. Y., 2004. Targeting the Minimum Water Flowrate Using Water Cascade Analysis Technique. *AIChE Journal,* 50(12), pp. 3169-3183.

McCormick, G. P., 1976. Computability of global solutions to factorable nonconvex programs: part1-Convex underestimating problems. *Mathematical Programming,* Volume 10, pp. 147-175.

Meyer, C. A. & Floudas, C. A., 2005. Global Optimisation of a Combinatorially Complex Generalised Pooling Problem. *AIChE Journal,* 52(3), pp. 1027-1037.

Misener, R. & Floudas, C. A., 2010. Global Optimisation of Largr-Scale Generalised Pooling Problems: Quadratically Constrained MINLP Models. *Industrial and Engineering Chemistry Research,* Volume 49, pp. 5424-5438.

Ng, D. K. S., Foo, D. C. Y. & Tan, R. R., 2007. Targeting for total Water Network. 1. Waste Stream Identification. *Industrial and Engineering Chemistry Research,* Volume 46, pp. 9107-9113.

Nowak, I., 2005. *(International Series of Numerical Mathematics 152) -Relaxation and Decomposition Methods for Mixed Integer Nonlinear Programming.* Basel: Birkhauser Verlag.

Ponce-Ortega, J. M., El-Halwagi, M. M. & Jimenez-Gutierrez, A., 2010. Global Optimisation for the Synthesis of Property-based Recycle and Reuse Networks Including Environmental Constraints. *Computers and Chemical Engineering,* Volume 34, pp. 318-330.

Poplewski, G. & Jezowski, J., 2007. A simultaneous approach for designing optimal wastewater treatment network. *Chemical Engineering Transcations,* Volume 12, pp. 321-326.

Poplewski, G., Walczyk, K. & Jezowski, J., 2010. Optimisation-based method for calculating water networks with user specified characteristics. *Chemical Engineerng Research and Design,* Volume 88, pp. 109-120.

Pörn, R., Bjork, K.-M. & Westerlund, T., 2008. Global solution of optimisation problems with signomial parts. *Discrete Optimisation*, Volume 5, pp. 108-120.

Pörn, R., Harjunkoski, I. & Westerlund, T., 1999. Convexification of different classes of non-convex MINLP. *Computer and Chemial Engineering,* Volume 23, pp. 439-448.

Quesada, I. & Grossmann, I. E., 1995. Global Optimisation of Bilinear Process Networks with Multicomponent Flows. *Computers and Chemical Engineering*, 19(12), pp. 1219-1242.

Rangaiah, G. P. & Wei, T. K. eds., 2010. *Advances in Process Systems Engineering: Stochastic Global Optimisation, Techniques and Applications in Chemical Engineering.* Toh Tuck, Singapore: World Scientific Publishing Co. Pte. Ltd..

Ryoo, H. S. & Sahinidis, N. V., 1996. A Branch and Reduce Approach to Global Optimisation. *Journal of Global Optimisation,* Volume 8, pp. 107-138.

Sachidnanda , M. & Rahimifard, S., 2012. *Reduction of Water Consumption within Manufacturing Application.* Berkeley, CIRP.

Saif, Y., Almansoori, A. & Elkamel, A., 2013. Wastewater Minimisation in Pulp and Paper Industries through Energy-Efficient Membrane Processes. *Chemical Engineering Technology,* 36(3), p. 419–425.

Salveski, M. & Bagajewicz, M., 2003. On the necessary conditions of optimality of water utiliztion systems in process plants with multiple contaminants. *Chemical Engineering Science,* Volume 58, pp. 5349-5362.

Sharma, S. K. & Sanghi, R., 2013. *Wastewater Reuse and Management.* London: Springer Science + Business Media Dordrecht.

Sherali, H. D. & Alameddine, A., 1992. A New Reformulation-Linearisation Technique for Bilinear Programming Problems. *Journal of Global Optimisation,* Volume 2, pp. 379-410.

Still, C. & Westerlund, T., 2010. A linear programming-based optimisation algorithm for solving nonlinear programming problems. *European Journal of Opertional Research,* Volume 200, pp. 658-670.

Strathmann, H., 2010. Electrodialysis, a mature technology with a multitude of new applications. *Desalination,* Volume 264, pp. 268-288.

Takama, N., Kuriyama, T., Shiroko, K. & Umeda, T., 1980. Optimal Water Allocation in a Petroleum Refinery. *Computers and Chemical Engineering,* Volume 4, pp. 251-258.

Tan, R. R., Ng, D. K. S., Foo, D. C. Y. & Aviso, K. B., 2009. A superstructure model for the synthesis of single-contaminant water networks with partitioning regenerators. *Process Safety and Environmental Protection,* Volume 87, pp. 197-205.

Tan, Y. L., Manan, Z. A. & Foo, D. C. Y., 2007. Retrofit of Water Network with Regeneration using Water Pinch Analysis. *Trans IChemE, Part B, Safety and Environmental Protection,* 85(B4), pp. 305-317.

Tawarmalani, M. & Sahinidis, N. V., 2004. Global optimisation of mixed-integer nonlinear programs: A theoretical and computational study. *Mathematical Programming,* Volume 99, pp. 563-591.

Teles, J., Castro, P. M. & Novais, A. Q., 2008. LP-based solution strategies for the optimal design of industrial water networks with multiple contaminants. *Chemical Engineering Science,* Volume 63, pp. 376-394.

Tsiakis, P. & Papageorgiou, L. G., 1995. Optimal design of an electrodialysis brackish water desalination plant. *Desalination,* Volume 173, pp. 173-186.

Tsiakis, P. & Papageorgiou, L. G., 2005. Optimal design of an electrodialysis brackish water desalination planyt. *Desalination,* Volume 173, pp. 173-186.

Walczyk, K. & Jezowski, J., 2008. *A single stage approach for designing water networks with multiple contaminants.* Rzeszów, Elsevier B.V., pp. 719-724.

Wang , Y. P. & Smith, R., 1994a. Wastewater Minimisation. *Chemical Engineering Science,* 49(7), pp. 981-1006.

Wang, L. K., Chen, J. P., Hung, Y.-T. & Shammas, N. K. eds., 2011. *Membrane and Desalination Technologies.* New York: Springer Science + Business Media LLC.

Wang, Y.-P. & Smith, R., 1994b. Design of Distributed Effluent Treatment Systems. *Chemical Engineering Science,* 19(18), pp. 3127-3145.

Westerlund, T. & Petterson , F., 1995. An Extended Cutting Plane Method for Solving Convex MINLP Problems. *Computers and Chemical Engineering,* Volume 19, pp. S131-S136.

Yang, L., Salcedo-Diaz, R. & Grossmann, I., 2014. Water Network Optimisation with Wastewater Regeneration Models. *Industrial & Engineering Chemistry Research,* 22 September, Volume 53, pp. 17680-17695.

Zamora, J. M. & Grossmann, I. E., 1998. Continuous global optimisation of structured process systems models. *Computers and Chemical Engineering,* 22(12), pp. 1749-1770.

Zeman, L. J. & Zydney, A. L., 1996. *Microfiltration and Ultrafiltration: Principles and Applications.* New York: Marcek Dekker Inc.

CHAPTER 3

Optimisation Model

3.1 Introduction

This chapter concerns the development of the optimisation model for a water network problem. Detailed mathematical relations and formulations are presented. A source-regenerator-sink framework is adopted. A superstructure approach that considers the water sources sinks and regeneration subnetwork simultaneously was used to formulate the water network problem considered in this work.

3.2 Superstructure Representation

The superstructure presented in this work is a set of all the feasible solutions to the optimisation problem. It includes all the feasible interconnections between different units in the water-regeneration network and is presented in Figure 3.1. This representation is an extension of the work by Khor et al. (2011). It includes a regeneration subnetwork as part of the water network. A closer look at this section of the network shows that provisions have been made for both parallel and series connection of regenerators as well as allowance for local recycle of regenerator products back to the same regenerator feed. These provisions allow for a complete synthesis within the regeneration subnetwork and water network.

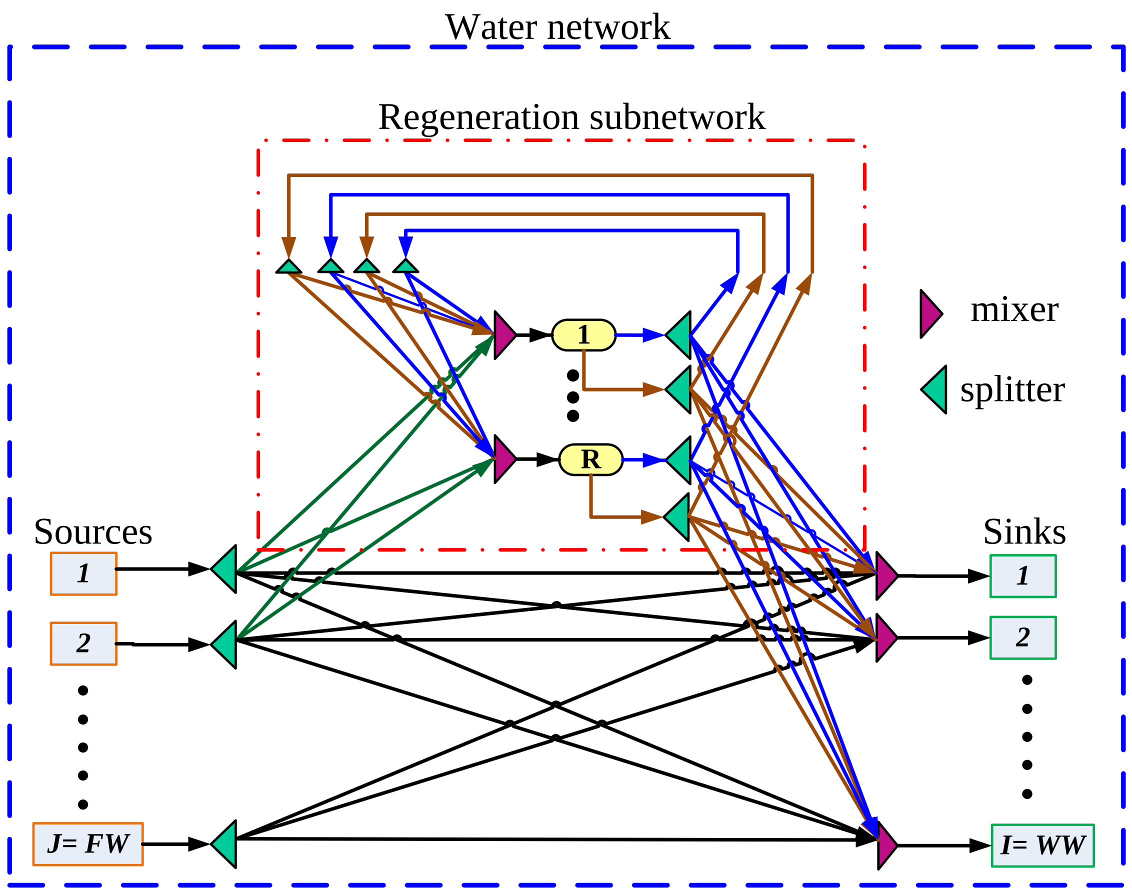


Figure 3.1: Superstructure representation of the water network.

3.3 Mechanistic ED regeneration network model

This section presents a mechanistic model formulation for a detailed design of an electrodialysis regeneration unit based on Tsiakis and Papageorgiou, (1995) and Lee et al. (2002). Figure 3.2 illustrates a schematic representation of a typical electrodialysis unit and how the ion-exchange membranes are laid out in each unit. For computational simplicity one stage per regenerator is assumed.

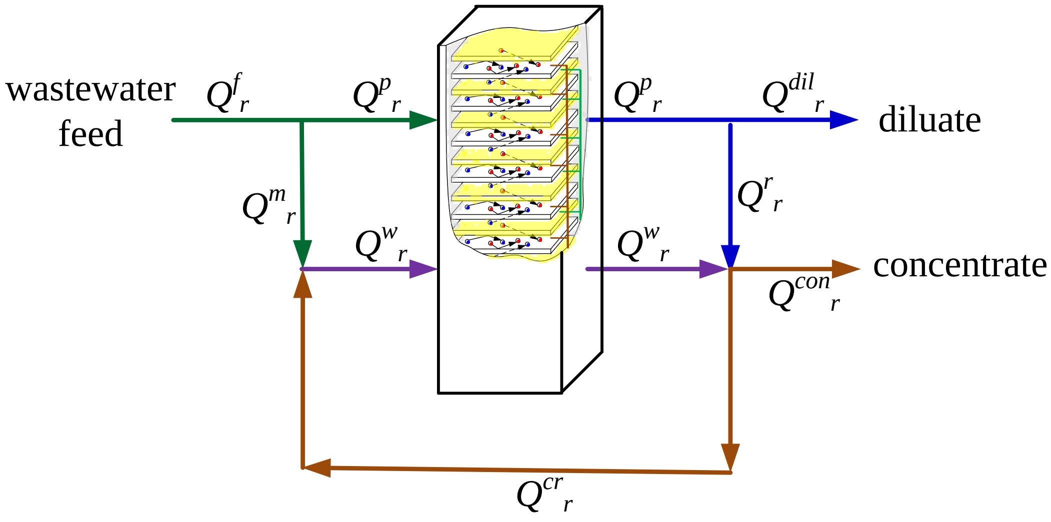


Figure 3.2: Schematic representation of a typical single-stage ED regenerator.

Assumptions are made in order to describe the plant using a set of mathematical equations describing its operation. The assumptions are as follows.

i) The fluids considered are Newtonian and have steady, fully developed, incompressible, laminar flow.

ii) The unit is operated under a co-current setup.

iii) Concentrate and diluate cells have identical geometry and flow patterns and changes in the ohmic resistance of the solutions are negligible (Tsiakis & Papageorgiou, 1995)

iv) The concentrations of the salt species are operated using molar equivalents.

v) Water transportation across the membrane is negligible compared to the concentrate and diluate stream flowrates(Tsiakis & Papageorgiou, 1995).

Material balances for each regenerator were conducted in accordance with Figure 3.2.

$$Q_r^f = Q_r^{dil} + Q_r^{con} \qquad \forall r \in R \qquad (3.1)$$

$$Q_r^f = Q_r^p + Q_r^m \qquad \forall r \in R \qquad (3.2)$$

$$Q_r^p = Q_r^{dil} + Q_r^r \qquad \forall r \in R \qquad (3.3)$$

$$Q_r^w = Q_r^m + Q_r^{cr} \qquad \forall r \in R \qquad (3.4)$$

$$Q_r^{con} = Q_r^w + Q_r^r - Q_r^{cr} \qquad \forall r \in R \qquad (3.5)$$

The corresponding contaminant balances are as follows:

$$Q_r^f C_r^f = Q_r^{con} C_r^{con} + Q_r^{dil} C_r^{dil} \qquad \forall r \in R \qquad (3.6)$$

$$Q_r^r C_r^{dil} + Q_r^w C_r^w = Q_r^{cr} C_r^{cr} + Q_r^{con} C_r^{con} \qquad \forall r \in R \qquad (3.7)$$

$$Q_r^m C_r^f + Q_r^{cr} C_r^{cr} = Q_r^w C_r^{wf} \qquad \forall r \in R \qquad (3.8)$$

$$Q_r^p C_r^f + Q_r^w C_r^{wf} = Q_r^p C_r^{dil} + Q_r^w C_r^w \qquad \forall r \in R \qquad (3.9)$$

To avoid the collapse of the membrane system due to pressure differences it is assumed that the immediate diluate and concentrate streams have the same flowrate, hence:

$$Q_r^p = Q_r^w \qquad \forall r \in R \qquad (3.10)$$

The recovery rate, R_r, determines the flowrate of the final diluate product stream and is defined as:

$$R_r = \frac{Q_r^{dil}}{Q_r^p} \qquad \forall r \in R \qquad (3.11)$$

The splitting rate, *M*, is defined as:

$$S_r = \frac{Q_r^p}{Q_r^f} \qquad \forall r \in R \qquad (3.12)$$

With regards to the design aspect of electrodialysis regenerator, important variables and physical parameters of the ED are incorporated in the mathematical relations that describe the performance of the regenerator. The electric current required to drive the electrodialysis process is given by:

$$I_r = \frac{zFQ_r^p C_r^{\Delta}}{\zeta N_r} \qquad \forall r \in R \qquad (3.13)$$

The practical current density is determined in terms of the linear velocity, v_r, using the following relationship:

$$i_r^{prac} = \varepsilon a^{LCD} C_r^{dil} (v_r)^{b^{LCD}} \qquad \forall r \in R \qquad (3.14)$$

The extent of desalination obtained by an electrodialysis unit is dependent on the membrane area, A_r which is given by:

$$A_r = \frac{\left[\ln \frac{C_r^w C_r^f}{C_r^{dil} C_r^{wf}} + \frac{\Lambda \rho C_r^{\Delta}}{\delta} \right] zFQ_r^p C_r^{dil}}{\left[\frac{C_r^{dil}}{C_r^w} + 1 + \frac{\Lambda C_r^{\Delta} \rho}{\delta} \right] i^{prac} \beta \zeta} \qquad \forall r \in R \qquad (3.15)$$

where, C_r^{Δ} is the concentration difference across a stage ($C_r^f - C_r^{dil}$). Q_r^p, is the diluate stream flowrate from the regenerator, *r*, which is expressed by constraint (3.16).

$$Q_r^p = N_r w \delta v_r \alpha \qquad \forall r \in R \qquad (3.16)$$

where, α is the spacer shadow factor. The required process path length for the ED stack can be expressed in terms of the membrane area, A_r, the cell width, *w*, and the number of cell pairs, N_r. in the following constraint:

$$L_r = \frac{A_r}{2wN_r} \qquad \forall r \in R \qquad (3.17)$$

The direct energy required for the process is dependent upon the voltage and current applied on each stack. The voltage applied can be expressed as follows:

$$U_r = \frac{Q_r^p C_r^\Delta zFN_r}{\zeta A_r}\left(\frac{\ln \frac{C_r^w C_r^f}{C_r^{dil} C_r^{wf}}}{\Lambda C_r^\Delta} + \rho\right) \qquad \forall r \in R \qquad (3.18)$$

The specific energy required for desalination is defined by constraint (3.19).

$$E_r^{spec} = \frac{U_r I_r}{Q_r^{dil}} \qquad \forall r \in R \qquad (3.19)$$

The specific pumping energy, E_r^{pump}, required for the process is directly linked to the pressure drop, ΔP_r, for laminar flow across the unit and is given by:

$$E_r^{pump} = \frac{\Delta P_r k^{tr}}{\eta} \qquad \forall r \in R \qquad (3.20)$$

where,

$$\Delta P = \frac{12 v_r \mu L_r}{\delta^2} \qquad \forall r \in R \qquad (3.21)$$

The regeneration network involves both capital and operational costs. The representative total annualised cost (*TAC*) function for the regeneration network is given by constraint (3.22). This function is included in the overall objective function of the water network, such that the energy consumption and subsequent cost of regeneration are minimised in conjunction with water consumption. To further improve flexibility, the model is enabled to only select the necessary regenerators that result in an optimal solution. This is achieved by prefixing the *TAC* function with a binary variable, y_r^{ED} which becomes zero when the respective unit is not activated.

$$TAC_r = y_r^{ED}\left[A_r\left(\frac{k^{mb}}{n}\right)+t^d k^{el} Q_r^{dil}\left(E_r^{spec}+E_r^{pump}\right)\right] \qquad \forall r \in R \qquad (3.22)$$

3.4 Water Balances

To ensure connectivity between the regeneration network, the sources and the sinks, water balances are established based on the superstructure presented in Figure 3.1.

3.4.1 Source balance

Figure 3.3 shows a schematic representation of how the water from a source splits into the different streams.

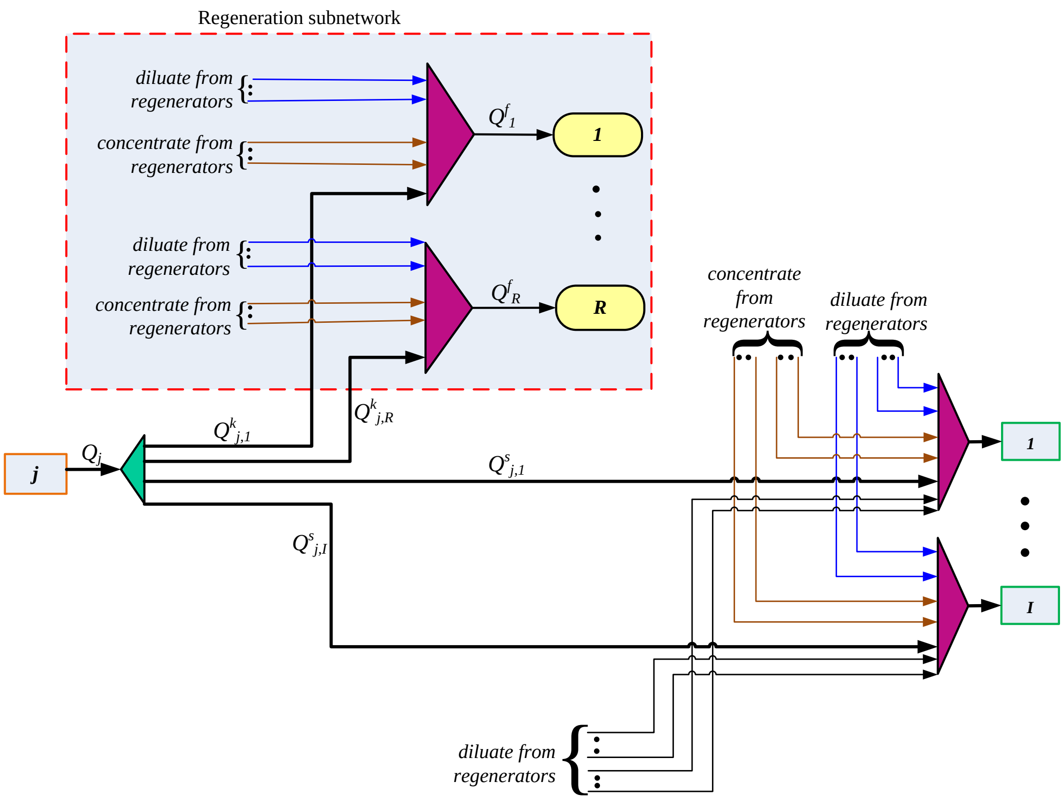


Figure 3.3: Schematic representation of a water source.

The flow balance for the source is modelled as:

$$Q_j = \sum_{r=1}^{R} Q_{j,r}^{k} + \sum_{i=1}^{I} Q_{j,i}^{s} \qquad \forall j \in J \tag{3.23}$$

The balance for the freshwater source is modelled in a similar way.

3.4.2 Regeneration network water balances

Figure 3.4 is a schematic representation of how a single regeneration unit is connected to the rest of the water network. The diagram shows the streams that feed into the individual regenerators in the subnetwork as well as the corresponding exit streams.

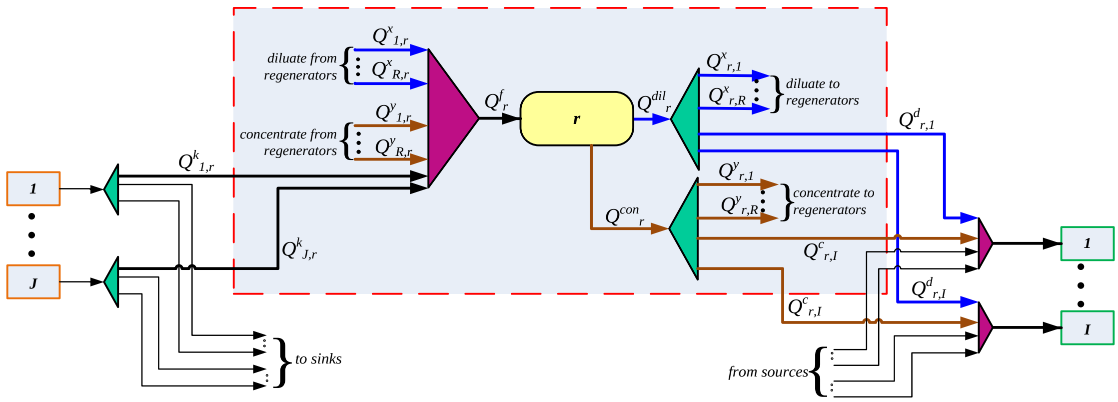


Figure 3.4: Schematic representation of the regeneration network.

Based on Figure 3.4, the water balance around the mixer preceding each regenerator can be modelled as:

$$Q_r^f = \sum_{r'=1}^{R} Q_{r',r}^{x} + \sum_{r'=1}^{R} Q_{r',r}^{y} + \sum_{j=1}^{J} Q_{j,r}^{k} \qquad \forall r \in R \tag{3.24}$$

Depending on the design of the regenerator, each regenerator has a limit to the amount of contaminant that it can tolerate. In this regard, the corresponding contaminant balance for the regenerator feed was modelled as:

$$S_r^U \leq \frac{\sum_{r'=1}^{R} Q_{r',r}^{x} C_{r'}^{dil} + \sum_{r'=1}^{R} Q_{r',r}^{y} C_{r'}^{con} + \sum_{j=1}^{J} Q_{j,r}^{k} C_j}{Q_r^f} \qquad \forall r \in R \qquad (3.25)$$

Similarly, the water balances for the two splitters connected to the regenerator diluate and concentrate streams are given by constraints (3.26) and (3.27) respectively.

$$Q_r^{dil} = \sum_{r'=1}^{R} Q_{r,r'}^{x} + \sum_{i=1}^{I} Q_{r,i}^{d} \qquad \forall r \in R \qquad (3.26)$$

$$Q_r^{con} = \sum_{r'=1}^{R} Q_{r,r'}^{y} + \sum_{i=1}^{I} Q_{r,i}^{c} \qquad \forall r \in R \qquad (3.27)$$

3.4.3 Sink water balance

Figure 3.5 shows a schematic representation of how streams from different units mix into a particular water sink.

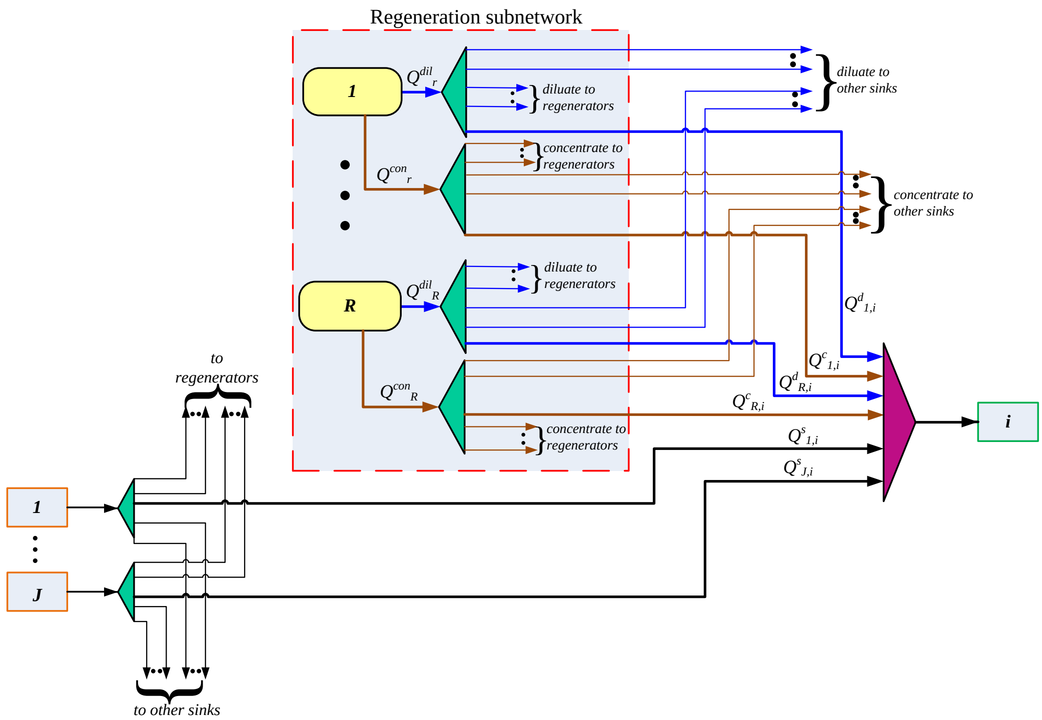


Figure 3.5: Schematic representation of a water sink.

The flow balance for the sink is modelled as:

$$Q_i^b = \sum_{r=1}^{R} Q_{r,i}^d + \sum_{r=1}^{R} Q_{r,i}^c + \sum_{j=1}^{J} Q_{j,i}^s \qquad \forall i \in I \tag{3.28}$$

The balance for the wastewater sink is modelled in a similar way. The maximum allowable load that each sink tolerates has to be taken into account. As such the corresponding contaminant balance for each sink can be modelled as:

$$C_i^U \geq \frac{\sum_{r=1}^{R} Q_{r,i}^d C_r^{dil} + \sum_{r=1}^{R} Q_{r,i}^c C_r^{con} + \sum_{j=1}^{J} Q_{j,i}^s C_j +}{Q_i^b} \qquad \forall i \in I \tag{3.29}$$

3.5 Logical constraints

To ensure that a diluate stream and a concentrate stream from the same regenerator are not re-mixed in a single sink or recycled into the same regenerator, the following constraints are introduced. $y_{r,i}^d$ and $y_{r,i}^c$ are binary variables that indicate the existence of diluate and concentrate streams while $y_{r,r'}^x$ and $y_{r,r'}^y$ denote diluate and concentrate recycle streams respectively.

$$y_{r,i}^d + y_{r,i}^c = 1 \qquad \begin{array}{l}\forall r \in R \\ \forall i \in I\end{array} \tag{3.30}$$

$$y_{r,r'}^x + y_{r,r'}^y = 1 \qquad \forall r, r' \in R \tag{3.31}$$

To ensure that the maximum flowrates that can be accommodated by the piping are not exceeded, appropriate logical constraints are also included. The constraints are such that upper and lower bounds are allocated to all the flowrates. These bounds are chosen based on practically feasible flowrates, such that any stream with a flowrate beyond these limits is not allowed to exist. This is achieved by the introduction of binary variables according to constraints (3.32) to (3.38).

$$y^{s}_{j,i} \cdot S^{U} \leq Q^{s}_{j,i} \leq y^{s}_{j.i} \cdot S^{L} \qquad \forall j \in J \quad \forall i \in I \qquad (3.32)$$

$$y^{k}_{j,r} \cdot K^{U} \leq Q^{k}_{j,r} \leq y^{k}_{j.r} \cdot K^{L} \qquad \forall j \in J \quad \forall r \in R \qquad (3.33)$$

$$y^{d}_{r,i} \cdot D^{U} \leq Q^{d}_{r,i} \leq y^{d}_{r.i} \cdot D^{L} \qquad \forall r \in R \quad \forall i \in I \qquad (3.34)$$

$$y^{c}_{r,i} \cdot C^{U} \leq Q^{c}_{r,i} \leq y^{c}_{r.i} \cdot C^{L} \qquad \forall r \in R \quad \forall i \in I \qquad (3.35)$$

$$y^{x}_{r,r'} \cdot X^{U} \leq Q^{x}_{r,r'} \leq y^{x}_{r,r'} \cdot X^{L} \qquad \forall r, r' \in R \qquad (3.36)$$

$$y^{y}_{r,r'} \cdot Y^{U} \leq Q^{y}_{r,r'} \leq y^{y}_{r,r'} \cdot Y^{L} \qquad \forall r, r' \in R \qquad (3.37)$$

$$y^{ED}_{r} \cdot E^{U} \leq Q^{s}_{r} \leq y^{ED}_{r} \cdot E^{L} \qquad \forall r \in R \qquad (3.38)$$

3.6 The objective function

The objective is to minimise the total annualised cost of the water network, which comprises the freshwater cost, wastewater treatment cost, annualised regeneration cost, as well as the capital and operating cost of piping. To account for capital and operational cost of piping, the length of pipe run, material of construction and linear velocities within the pipes were considered. The formulation of the objective function is expressed in constraint (3.39).

$$\min\left\{\begin{array}{l}\left(C^{FW}FW+C^{WW}WW\right)t^{d}+\sum_{r=1}^{R}TAC_{r}+\\ A^{f}\left[\begin{array}{l}\sum_{j=1}^{J}\sum_{i=1}^{I}D_{j,i}^{s}\left(\frac{pQ_{j,i}^{s}}{3600\cdot v}+q\cdot y_{j,i}^{s}\right)+\sum_{r=1}^{R}\sum_{i=1}^{I}D_{r,i}^{c}\left(\frac{pQ_{r,i}^{c}}{3600\cdot v}+q\cdot y_{r,i}^{c}\right)+\\ \sum_{r=1}^{R}\sum_{i=1}^{I}D_{r,i}^{d}\left(\frac{pQ_{r,i}^{d}}{3600\cdot v}+q\cdot y_{r,i}^{d}\right)+\sum_{r=1}^{R}\sum_{r'=1}^{R}D_{r,r'}^{x}\left(\frac{pQ_{r,r'}^{x}}{3600\cdot v}+q\cdot y_{r,r'}^{x}\right)+\\ \sum_{r=1}^{R}\sum_{r'=1}^{R}D_{r,r'}^{y}\left(\frac{pQ_{r,r'}^{y}}{3600\cdot v}+q\cdot y_{r,r'}^{y}\right)+\sum_{j=1}^{J}\sum_{r=1}^{R}D_{j,r}^{k}\left(\frac{pQ_{j,r}^{k}}{3600\cdot v}+q\cdot y_{j,r}^{k}\right)\end{array}\right]\end{array}\right\} \tag{3.39}$$

where $A^{f}=\frac{m(1+m)^{n}}{(1+m)^{n}-1}$ is an annualisation factor. It is assumed that all the pipes share the same p and q parameter properties, stream velocity, v, and 1-norm Manhattan Distance. The resulting mathematical model is a mixed integer nonlinear programming (MINLP) problem that was solved using GAMS/DICOPT with CPLEX as the MILP solver and CONOPT 3 as the NLP solver. BARON was used to solve the RMINLP problem for which the results were used as a starting point for DICOPT. The type of computer processor used is an Intel ® Core ™ i7-4770 CPU @ 3.40 GHz.

3.7 Nomenclature

J = {j|j= water sources}

I = {i|i = water sinks}

R = {r|r = regenerators}

Parameters

LR_r liquid recovery for regenerator, r

F Faraday constant

w cell width

z valence

a^{LCD} LCD constant

b^{LCD} LCD constant

k^{tr} conversion factor

ζ current utilisation

α spacer shadow factor

δ cell thickness

ρ total membrane resistance

β volume factor

λ equivalent conductance

μ solution viscosity

η pumping efficiency

ε safety factor

k^{el} cost of electricity

k^{mb} cost of membrane

C^{FW} freshwater cost

C^{WW} wastewater treatment cost

n maximum equipment life

t^{d} operating time per year

p parameter for carbon steel piping

q parameter for carbon steel piping

m interest rate per year

v pipe linear velocity

$D^{s}_{j,i}$ Manhattan distance between source, *j* and sink, *i*

$D^{d}_{r,i}$ Manhattan distance between regenerator, *r* and sink, *i*

$D^{y}_{r,r'}$ Manhattan distance between regenerators *r* and *r'*

$D^{k}_{j,r}$ Manhattan distance between source, *j* and regenerator, *r*

Continuous variables

TAC_r total annualised cost for regenerator, *r*.

A_r membrane area required by regenerator *r*.

E^{spec}_r specific desalination energy required by regenerator *r*.

E^{pump}_r specific pumping energy required by regenerator *r*.

I_r electric current required by regenerator *r*.

L_r Stack length

v_r Linear flow velocity, at stage s

U_r Voltage applied

ΔP_r Pressure drop across the regenerator

Q^{f}_r Regenerator feed flowrate

R_r Recovery rate for regenerator, *r*

S_r Splitting rate for regenerator, *r*

Q^{dil}_r Final diluate stream flowrate of regenerator, *r*

Q_r^p Diluate stream flowrate for regenerator, *r*

Q_r^w Concentrate stream flowrate for regenerator, *r*

Q_r^{cr} Concentrate stream recycle flowrate for regenerator, *r*

Q_r^r Recycle stream flowrate for regenerator, *r*

Q_r^{con} Final concentrate flowrate for regenerator, *r*

$Q_{r,i}^d$ Diluate flowrate to sink, *i*

$Q_{r,i}^c$ Concentrate flowrate to sink, *i*

Q_j Source flowrate

$Q_{j,r}^k$ Flowrate from source, *j* to regenerator, *r*

$Q_{j,i}^s$ Flowrate from source, *j* to sink, *i*

$Q_{r,r'}^x$ Recycle from diluate stream to regenerator feed

$Q_{r,r'}^y$ Recycle from concentrate stream to regenerator feed

Q_i^b Sink, *i*, flowrate requirements

FW Freshwater flowrate

WW Wastewater flowrate

C_r^f Regeneration feed concentration for regenerator, *r*

C_r^{wf} Concentration of feed concentrate stream for regenerator, *r*

C_r^{cr} Concentration of recycling concentrate for regenerator, *r*

C_r^w Concentration of concentrate waste stream for regenerator, *r*

C_r^{dil} Diluate contaminant concentration

C_r^{con} Concentrate contaminant concentration

S_r^U Maximum allowable regenerator concentration

C_j Source concentration of

C_i^U Maximum allowable sink concentration

RR_r Removal ratio for regenerator, *r*

Integer variables

N_r Number of cell pairs per regenerator, *r*

Binary variable

$y_r^{ED} = \begin{cases} 1 \leftarrow \text{if regenerator } r \text{ exists} \\ 0 \leftarrow \text{otherwise} \end{cases}$

$y_{r,i}^{d} = \begin{cases} 1 \leftarrow \text{piping exists between reg.diluate and sink, } i \\ 0 \leftarrow \text{otherwise} \end{cases}$

$y_{r,i}^{c} = \begin{cases} 1 \leftarrow \text{piping exists between reg. concentrate and sink, } i \\ 0 \leftarrow \text{otherwise} \end{cases}$

$y_{r,r'}^{x} = \begin{cases} 1 \leftarrow \text{recycle exists from regenerator diluate to reg. } r \\ 0 \leftarrow \text{otherwise} \end{cases}$

$y_{r,r'}^{y} = \begin{cases} 1 \leftarrow \text{recycle exists from reg. concentrate to reg. } r \\ 0 \leftarrow \text{otherwise} \end{cases}$

$y_{j,r}^{k} = \begin{cases} 1 \leftarrow \text{piping exists between source, } j \text{ and regenerator, } r \\ 0 \leftarrow \text{otherwise} \end{cases}$

$y_{j,i}^{s} = \begin{cases} 1 \leftarrow \text{piping exists between source } j \text{ and sink, } i \\ 0 \leftarrow \text{otherwise} \end{cases}$

3.8 References

Khor, C.S., Foo, D.C.Y., El-Halwagi, M.M. and Tan R. R., Shah N. (2011) 'A Superstructure Optimisation Approach for Membrane Separation-Based Water Regeneration Network Synthesis with Detailed Nonlinear Mechanistic Reverse Osmosis Model', *American Chemical Society*, no. 50, pp. 13444-13456.

Lee, H.-J., Safert, F., Strahmann, H. and Moon, S.-H. (2002) 'Designing of an electrodialysis desalination plant', *Desalination*, vol. 142, pp. 267-286.

Tsiakis, P. and Papageorgiou, L.G. (1995) 'Optimal design of an electrodialysis brackish water desalination plant', *Desalination*, vol. 173, pp. 173-186.

CHAPTER 4

Results and Discussion

4.1 Introduction

In this chapter, the mathematical model that was developed in the previous chapter is applied to an industrial case study to demonstrate its applicability. The case study was carefully chosen so as to accommodate the limitations of the model to systems with ionic contaminants. The benefits of using a detailed model are clearly revealed when different scenarios are considered.

4.2 Case study

The mathematical model developed is applied to a literature based pulp and paper plant case study (Chew et al., 2008). This case study was chosen mainly because the industry is known to produce a lot of ionic effluent making it possible to apply the electrodialysis regenerators incorporated in the model. This wastewater comes mainly from the bleaching section of the plant, where water is contaminated with chlorides and chlorates. Figure 4.1 shows a schematic of a typical pulp and paper plant.

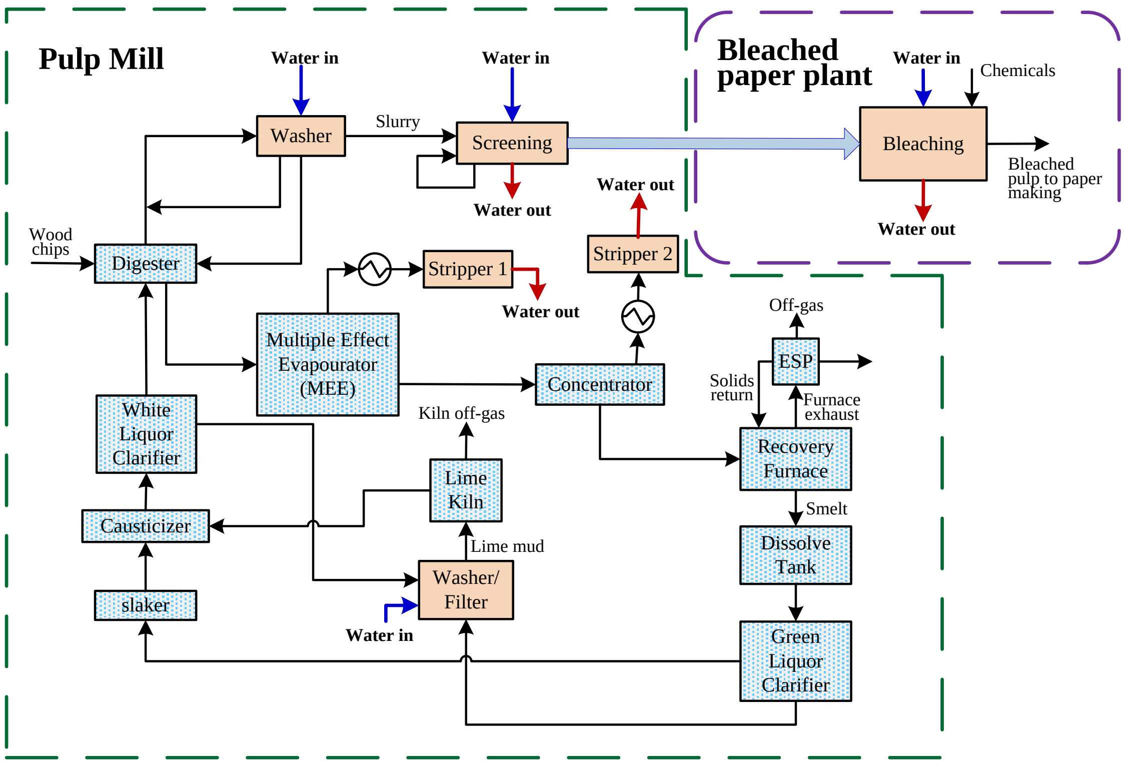


Figure 4.1: Typical pulp and paper plant (Chew et al., 2008).

The pulp and paper industry is known to involve miscible water networks such as water-water systems, whereby mixing streams lose their identities as they mix and water gains and losses are encountered. This renders the fixed-flowrate framework adopted in the model ideal for this particular plant (Poplewski et al., 2010).

Table 4.1: Limiting data for the water sources and sinks.

Source, *j*				Sinks, *i*			
j	*Unit*	*Flowrate (t/h)*	*Conc. (mg/L)*	*i*	*Unit*	*Flowrate (t/h)*	*Max. conc (mg/L)*
1	washer	890.1	0.001	1	Stripper 1	1399.5	34.0
2	Screening	145.0	269.6	2	Screening	145.0	0
3	Washer/filter	102.4	0	3	Stripper 2	576.2	0.370
4	Bleaching	3099.0	499.8	4	Bleaching	3099.0	0.014
5	Freshwater	∞	0	5	Wastewater	∞	398.3

Table 4.1 shows the plant limiting data in terms of flowrate and contaminant (Cl^-) concentration for the sources and sinks amenable for wastewater recycle and reuse. According to this data, the plant water network involves five water sources including the freshwater source and five sinks including the wastewater discharge. Process and economic data for detailed design of ED units and the case study is given in Table 4.2. Data on the Manhattan distances between units is presented in Table 4.3

Table 4.2: Process and economic data for the case study.

Parameter	**Value**
liquid recovery, *LR*	0.7
Faraday constant, *F*	9.65×10^7 As/keq
cell width*, *w*	0.42 m
valence, *z*	1
LCD constant*, a^{LCD}	25000
LCD constant*, b^{LCD}	0.5
conversion factor, k^{tr}	27.2
current utilisation*, ζ	0.9
spacer shadow factor*, α	0.8
cell thickness*, δ	0.65 mm
total membrane resistance*, ρ	0.0007 Ωm^2
volume factor*, β	0.7
equivalent conductance*, λ	10.5
pumping efficiency*, η	0.7
safety factor*, ε	0.7
cost of electricity*, k^{el}	$0.12/kWh
cost of membrane*, k^{mb}	$150/m²
freshwater cost†, C^{FW}	$1/m³
wastewater treatment cost†, C^{WW}	$1/m³
maximum equipment life, *n*	5yrs
operating time per year, t^d	330 days
parameter for carbon steel piping†, *p*	7200
parameter for carbon steel piping†, *q*	250
interest rate per year†, *m*	0.05
pipe linear velocity†, *v*	1 m/s

* Tsiakis and Papageorgiou, (1995)
† Khor et al. (2014)

Table 4.3: Data on Manhattan distance (in m) for the case study.

Source	Sink					Regeneration unit	
	i_1	i_2	i_3	i_4	i_5	r_1	r_2
j_1	50	60	70	50	75	50	60
j_2	60	50	60	55	70	65	50
j_3	50	80	50	45	65	60	55
j_4	55	60	70	60	50	50	60
j_5	50	65	50	65	55	55	50
Regeneration unit							
r_1	80	70	80	50	55		
r_2	70	90	75	55	60		

4.2.1 Scenarios considered

To ensure a detailed analysis of the model, four scenarios were considered. Scenario 1 was water integration without regeneration. In this scenario, only direct reuse and recycle between water-using units were considered. This is considered to be the base case for which all other cases are compared to.

Scenario 2 is the case where water integration with regeneration involving two detailed ED regenerators was considered. However in this case, series connections and recycles within the regeneration subnetwork were forbidden just as in the case presented by Khor et al. (2011). This is achieved by eliminating the first and second terms on the right hand side of Eq. 3.24 as well as the first terms on the right hand side of Eq. 3.26 and Eq. 3.27. This implies that a product stream from one regenerator cannot be connected to the feed of any other regenerator including that same regenerator. Note that in this case, the system had freedom to choose only the necessary regenerators. For this scenario, the removal ratio is fixed.

Scenario 3 considers a water network with one detailed ED regenerator with capabilities of recycle within the regeneration subnetwork. A connection between either a permeate stream or a reject stream and the feed stream can be made. Within this scenario two cases were considered, namely; a case where the removal ratio of the regenerator is fixed at 0.733 and the case where it is variable. For the case where the removal ratio is fixed, no basis is used for the selection of this removal ratio. An arbitrary value is chosen.

Scenario 4 is similar to scenario 3 except that it has the capability of using two regenerators. Fixed removal ratios at 0.733 and 0.950 for the first and second regenerators respectively are chosen for the fixed removal ratio case. Here again values for the removal ratios were chosen arbitrarily.

4.2.2 Variable Bounds

All models were formulated as MINLP problems in the optimisation platform GAMS. Inspection of the models showed that they contain a lot of discrete variables (binary and integer variables) which offer high computational burden for the solvers. In order to cut down on CPU time, tight bounds based on physical inspection of industrial cases were imposed on some variables (Tsiakis & Papageorgiou, 1995). This includes bounds on the removal ratio, number of cell pairs, stack length and linear flow velocity within the regenerator units. Table 4.4 shows a list of the bounds imposed on the design variables for the ED units obtained from literature (Tsiakis & Papageorgiou, 1995).

Table 4.4: Typical values of operational parameters for ED units.

Design variable	**Typical values**
E_r^{spec}, kWh/m^3	< 15
v_r, m/s	0.01-0.4
L_r, m	0.7-1.6
N_r	50-5000
R_r	< 95%
RR	0.70-0.95

As for bounds on the freshwater intake and wastewater discharge flowrates, the flowrates obtained in scenario 1 were taken as the upper bound to these variables. Justification for this is based on the fact that, freshwater demands by water networks with regeneration ought to be less than the demands for the no regeneration cases; otherwise regeneration is eliminated resulting in the demands by scenario 1.

4.3 Results and Discussion

Table 4.5 shows the resultant model structures of the four scenarios considered and these statistically show the size of the model, the tolerances allowed for and the corresponding number of major and minor iterations it took the solver to obtain a solution.

Table 4.5: Model features of the scenarios considered.

	Scenario 1	**Scenario 2**	**Scenario 3**		**Scenario 4**	
	Base case	*Fixed RR**	*Fixed RR**	*Variable RR**	*Fixed RR**	*Variable RR**
No. of constraints	81	249	176	176	269	269
No. of continuous variables	68	202	146	147	218	220
No. of discrete variables	25	59	44	44	67	67
No. of major iterations	3	4	3	3	3	6
No. of minor iterations	90	967	415	340	728	3739
Tolerance	0	0.1	0.1	0.1	0. 1	0.1
CPU time (*s*)	0	312	8	72	6129	17230

**RR*-removal ratio

From Table 4.5 it is evident that the model was relatively complex owing to the large number of continuous and discrete variables as well as constraints. The problem size grows as we move from the base case where less piping interconnections are involved for a single regenerator and to multiple regenerators. The consequent increase in the number iterations and CPU time following a similar trend was expected.

Table 4.6 presents the optimum synthesis results for the four water network scenarios considered. For comparison's sake, quantities in freshwater intake and wastewater generation are analysed as well as the regeneration costs and total annualised costs of the entire network. Optimum removal ratios for the scenarios with variable removal ratios are also reported in Table 4.6.

Table 4.6: Optimum results for the scenarios considered.

	Scenario 1	Scenario 2	Scenario 3		Scenario 4	
		*Fixed RR**	*Fixed RR**	*Variable RR**	*Fixed RR**	*Variable RR**
Freshwater flowrate (*t/s*)	1.134	1.093	1.055	1.023	1.006	0.989
Wastewater generation (*t/s*)	0.861	0.820	0.782	0.750	0.733	0.716
Total water regenerated (*t/s*)	0	0.115	0.596	0.217	0.699	0.586
Regeneration cost (million $)	0	0.076	0.341	0.243	0.562	0.353
Total cost (million $)	56.9	54.7	52.7	50.8	50.2	48.9
Optimal *RR**	-	-	-	r_1= 0.867	-	r_1= 0.779 r_2= 0.770

**RR*-removal ratio

Following from the deductions made in preceding chapters about how the addition of regenerators in water networks can improve plant profitability by cutting on the amount of freshwater intake and wastewater generated, scenario 1 is expected to be the worst case scenario. Table 4.6 shows that indeed it is the least preferable of those considered.

On the other hand, as would be expected, Scenario 4 is the most desirable since it results in the lowest total network cost. It is noteworthy that for the proposed model in scenario 4, even though two regenerators were considered, the system is not limited to the two. It can be applied to more. In addition, caution must be taken not to conclude that the more regenerators used imply high profitable the plant. This is because there are a lot of trade-offs made between different factors during the optimisation process. As such there is always a limit to which the number of regenerators added can push to improve plant cost-effectiveness. The binary variables, y_r^{ED} , put in place to indicate the existence of a regenerator ensure that this standpoint is not overlooked. After optimisation only the necessary regenerators are selected.

Based on literature it is expected that the comparison between the fixed and variable removal ratio cases within each scenario would show the effectiveness of making the removal ratio variable over the other alternative (Yang et al., 2014). This is because since the technicalities of regeneration are included in the detailed model, the performance of the regenerator, dictated by the removal ratio, directly influences the quantity of wastewater to be treated. As such varying the removal ratio allows the optimiser to select both the performance and the quantity of water to be treated such that a better optimum is always guaranteed. The results prove that the ideology is correct.

Figure 4.2 to Figure 4.7 show the optimal network configuration and flowrates obtained according to the respective scenarios. All flowrates are reported in t/s. With regards to the structure of the network, it is evident from Figure 4.3 and Figure 4.7 as well as the economic results presented in Table 4.6 that by allowing the solver to choose the optimal configuration within the regeneration subnetwork in terms of recycles, series and parallel connections as well as making the number of regenerators required variable, there exist possibilities of obtaining better solutions rather than fixing them arbitrarily beforehand. In this way the designer gains a better understanding of the conditions under which the plant should operate and is better able to stipulate the required membrane characteristics to the manufacturer.

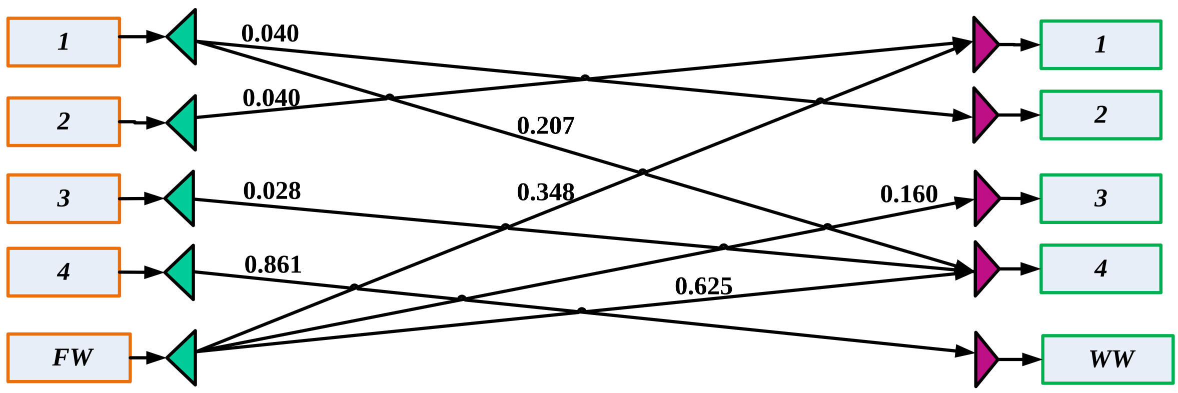


Figure 4.2: Optimum water network configuration for scenario 1.

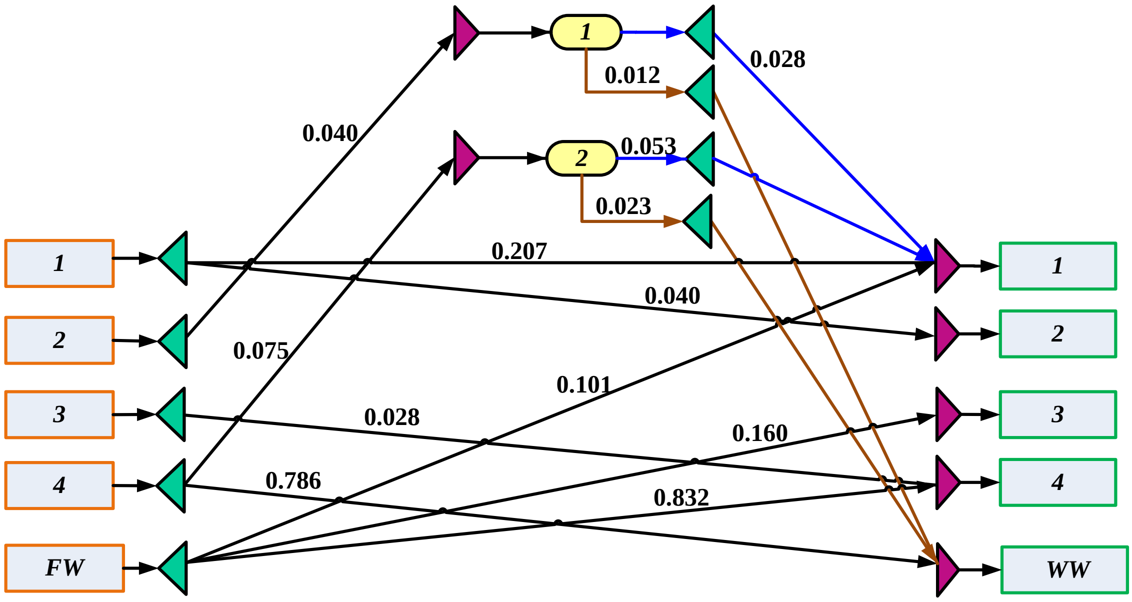


Figure 4.3: Optimum water network configuration for scenario 2.

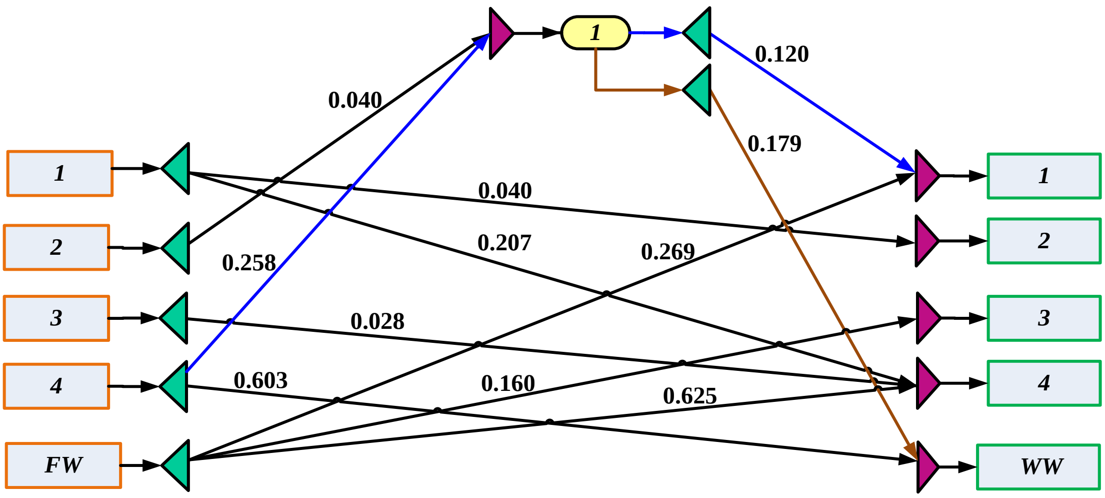


Figure 4.4: Optimum water network configuration for scenario 3 (fixed RR).

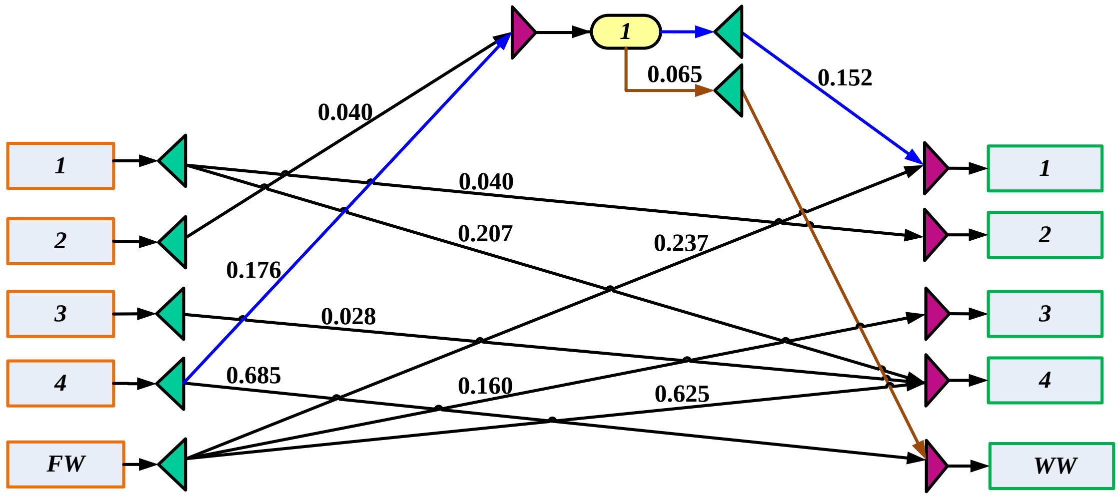


Figure 4.5: Optimum water network configuration for scenario 3 (variable RR).

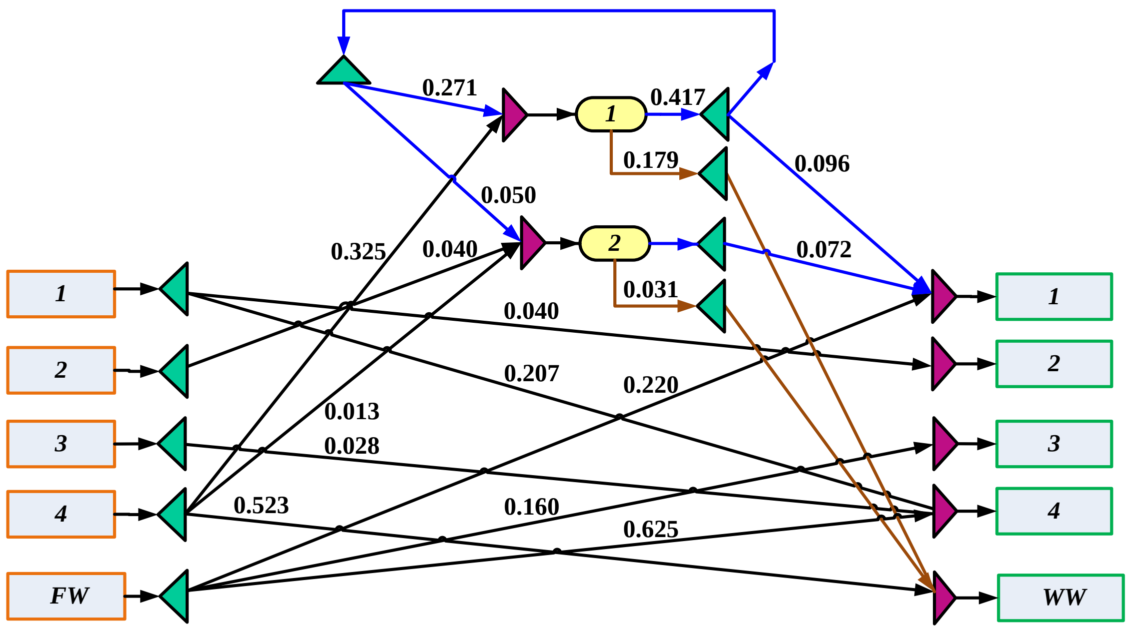


Figure 4.6: Optimum water network configuration for scenario 4 (fixed RR).

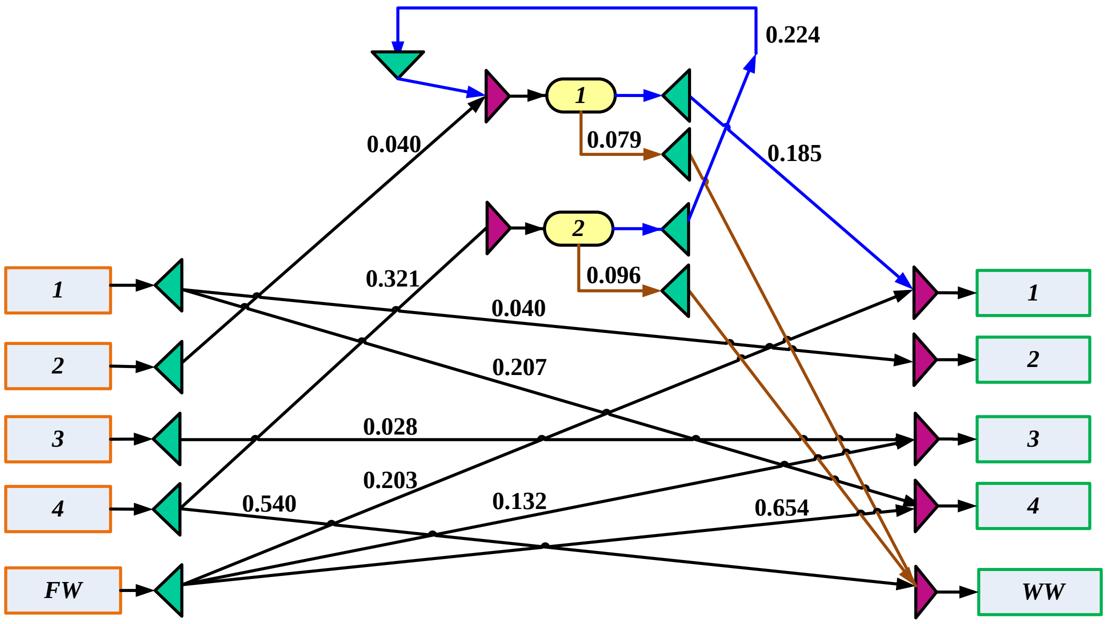


Figure 4.7: Optimum water network configuration for scenario 4 (variable RR).

Table 4.7 details the design results obtained for both regenerators. Careful inspection of the design features show that for the single regenerator case and for cases where the removal ratio was used, the maximum possible capacity of the regenerators in terms of number of membrane cell pairs in chosen. This is also apparent in the values of the linear velocities and stack length. This indicates the system's desire to expand its regeneration capacity. This is evident with Scenario 4 which has an extended regeneration capacity as indicated in Table 4.7.

Table 4.7: Optimum design results for the scenarios considered.

Variable	Scenario 2 Fixed RR r_1	Scenario 2 Fixed RR r_2	Scenario 3 Fixed RR r_1	Scenario 3 Variable RR r_1	Scenario 4 Fixed RR r_1	Scenario 4 Fixed RR r_2	Scenario 4 Variable RR r_1	Scenario 4 Variable RR r_2
N_r	729	1531	5000	5000	5000	5000	2880	4356
I_r (A)	13.8	19.9	28.3	21.3	31.9	6.1	18.8	27.6
A_r (m^2)	638	1284	6414	6720	6441	6720	3837	3921
L_r (m)	1.042	0.998	1.527	1.600	1.534	1.600	1.586	1.072
v_r (m/s)	0.185	0.165	0.4	0.145	0.4	0.069	0.309	0.247
U_r (V)	297	559	2809.27	1561	2816	1023	1412	1731
E_r^{spec} (J/s)	0.038	0.059	0.053	0.061	0.060	0.024	0.039	0.068
E_r^{pump} (J/s)	0.016	0.014	0.051	0.019	0.051	0.009	0.041	0.022
ΔP (kPa)	5.4	4.6	17.1	6.5	17.1	3.1	13.7	7.4
Q_r^f (kg/s)	0.040	0.075	0.596	0.217	0.596	0.103	0.27	0.32
RR_r	0.733	0.733	0.733	0.867	0.733	0.950	0.700	0.779

4.4 Conclusion

In this chapter the proposed model was applied on a literature case study to demonstrate its applicability. The results showed that the technicalities of regeneration directly influence the quantities and qualities of wastewater regenerated and are far from trivial when water regeneration networks are considered. Savings of up to 13% in freshwater intake, reduction of up to 16% in wastewater generation and a 14% saving in the total annualised cost compared to the worst case scenario of those considered were achieved. The optimal regenerator design suggests an installation of two regenerators, r_1 and r_2, one with 2880 cell pairs and the other with 4356, amounting to a total membrane area of 3800 m^2 and 3900 m^2 respectively.

4.5 References

Chew, I.M.L., Tan R., Ng D. K. S, Foo D. C., Majozi T. & Gouws J., 2008. Synthesis of Direct and Indirect Interplant Water Network. *American Chemical Society*, 47, pp.9485-96.

Khor, C.S., Foo, D.C.Y., El-Halwagi, M.M. & Tan R. R., Shah N., 2011. A Superstructure Optimisation Approach for Membrane Separation-Based Water Regeneration Network Synthesis with Detailed Nonlinear Mechanistic Reverse Osmosi Model. *American Chemical Society*, (50), pp.13444-56.

Poplewski, G., Walczyk, K. & Jezowski, J., 2010. Optimisation-based method for calculating water networks with user specified characteristics. *Chemical Engineerng Research and Design*, 88, pp.109-20.

Tsiakis, P. & Papageorgiou, L.G., 1995. Optimal design of an electrodialysis brackish water desalination planyt. *Desalination*, 173, pp.173-86.

Yang, L., Salcedo-Diaz, R. & Grossmann, I., 2014. Water Network Optimisation with Wastewater Regeneration Models. *Industrial & Engineering Chemistry Research*, 53, pp.17680-95

CHAPTER 5

Future Work

5.1 Introduction

The work presented in this dissertation has a number of limitations. Based on these shortcomings, the current chapter serves to offer scope for future work in the field of optimisation of water networks. The author recommends an extension of the work to include multiple regenerator technologies and to include consideration on contaminant accumulation within the regenerators as well as considerations on optimisation under uncertainty. Ways to improve computational time through efficient pre-processing are also suggested.

5.2 Multiple Regenerator Technologies

The regeneration subsystem considered in this work only looked at electrodialysis technology. Although the use of multiple membrane technology was implied through the use of variable regenerator performances, the dynamics of regeneration between two different membranes cannot be modelled in the same way. This is especially obvious for membranes which are based on different driving forces.

As highlighted earlier (Chapter 2), the mature membrane technologies for wastewater treatment are the pressure-driven membranes and electrodialysis (Judd, 2006). Considering that the current work has already dealt with electrodialysis, the same model may need to be modified for application on a different membrane, say ultrafiltration. As such, to fully capture the essence of multiple technologies, detailed models of pressure-driven membranes should be incorporated in the water network model to form an integrated multi-membrane water network.

Additionally, the use of electrodialysis technology limits the problem to cases where ionic contaminants are involved. The removal of non-ionic contaminants is equally important since these contaminants also pose detrimental impacts on the process operations and the environment. As a result, multiple technologies allow for the removal a variety of contaminants thereby making the contaminant removal more efficient and realistic.

5.3 Contaminant accumulation in regenerators

Within the regeneration subnetwork, we recall that local recycles were allowed for in the proposed model (Chapter 3). For instance, a permeate/reject stream from one regenerator could connect to the feed stream of that same regenerator. This has the desirable effect of further decreasing freshwater intake into the system and reducing wastewater generation for discharge into disposal site depending on the problem as indicated by the synthesis results presented in the previous chapter.

Contrary to that, literature has shown that these local recycles lead to contaminant accumulations in within the system (Chang & Li, 2005). This would not be a problem if the contaminants do not interfere with treatment processes or with plant operations; however this is hardly the case. For instance, some contaminants, when given enough time, react and adhere to the surface of the membranes thereby reducing the membrane efficiency and shortening the life of the membrane. As such, considerations on the accumulation of contaminants depending on the problem at hand need to be accounted for. This may include forbidding some streams to be recycled or including some pre-treatment stages prior to the electrodialysis treatment.

5.4 Optimisation under Uncertainty

Plant operations do not always run smoothly and at most instances they require continuous monitoring and control so as to obtain the desired outcomes. The same is true with process water networks. Process disturbances and changes in the quality of freshwater available, in mass loads/flowrates, in the performance of treatment units as well as in environmental regulations are common occurrences (Faria & Bagajewicz, 2011). When these fluctuations occur, control systems may result in variation of freshwater flowrates in which case the water minimising results originally intended may be undesirably altered (Feng et al., 2010). In light of this, it is important to address designs in water networks, especially for retrofit purposes, in a systematic way so as to deal with these uncertainties.

Optimisation under uncertainty, either based on flexibility, fuzzy programming or on stochastic programming, allows water network synthesis under both normal and disturbance conditions (Feng et al., 2010; Khor et al., 2014). Within the context of water network optimisation, extensive work on the subject has been presented in literature with possible suggestions on the use of buffer tanks and supplementary pipelines (Hung & Kim, 2011).

In the same context, planning models can be used for time-varying water network input data and can therefore be applied in cases where possible future process changes or alterations such as retrofits are apparent. (Faria & Bagajewicz, 2011). Numerous case studies to demonstrate the need to consider uncertain process conditions in the design of water networks have been presented (Khor et al., 2014).

5.5 Efficient Preprocessing

As was evident from the results presented in the previous chapter, the problem took a relatively long time to solve although powerful solvers were used. The time taken by a solver to report a solution to a given problem is largely dependent on the structure of the problem; that is nonlinearities, number of binary variables, continuous variables and constraints.

Most algorithms used to solve optimisation problems involve a preprocessing stage before the actual solution procedure begins. The basic idea in preprocessing is to reduce the problem size so as to reduce the data storage requirements and CPU time to solve the problem. Standard preprocessing techniques achieve this by reducing the number of variables and constraints by the elimination of redundant variables and constraints. Advanced methods also improve the scaling of the model and sparsity of the constraint matrix, strengthen the bounds on variables and detect the primal and dual infeasibility of the model.

The MILP community has benefited greatly from preprocessing since the concept has reached a high stage of maturity, however NLP and MINLP preprocessing is still lagging behind. As literature shows, global solvers need more than black-box function evaluation. They heavily rely on the delivery of structural information of algebraic expressions from the modelling languages (Busieck & Pruessner, 2003).

As such, the development and implementation of efficient preprocessing methods or schemes that are capable, in addition to the standard features, of identifying variables and constraints that impact the solution process the most and taking advantage of these to quickly give a solution is recommended. “Taking advantage” in this context may include imposing tight bounds on these variables and linearising respective terms and constraints before applying any algorithms. Literature also suggests the implementation of ‘open algorithms’ that allow users to adjust the algorithm to suit the problem at hand. For instance, the use of AIMMS-OA which is an open algorithm similar to GAMS/DICOPT (Busieck & Pruessner, 2003).

5.6 Conclusion

Mathematical programming is inherently theoretical and is highly dependent on empirical data available in literature especially for detailed designs. It aims to simulate reality by exploiting mathematical relations. The recommendations made in this chapter are aimed at making improvements on the proposed water network model in order to make it more comparable with real world. Recommendations on ways to improve the solution finding process in terms of reducing the computational time were also suggested.

5.7 References

Chang, C.-T. & Li, B.-H., 2005. Improved Optimisation Strategies forGenerating Practical Water-Usage and Treatment Network Structures. *Industrial and Engineering Chemistry Research,* Volume 44, pp. 3607-3618.

Faria, D.C. & Bagajewicz, M., 2011. Planning Model for the Design and/or Retrofit of Industrial Water Systems. *American Chemical Society*, 50, pp.3788-97.

Feng, X., Shen, R., Zheng, X. & Lu, C., 2010. Water Allocation Network Design Concerning Process Disturbance. *Industrial & Engineering Chhemistry Research*, 50, pp.3675-85.

Hung, S.W. & Kim, J.-K., 2011. Integrated water network Optimisation under Uncertainty. *Chemical Engineering Journal*, 175, pp.56-69.

Judd, S., 2006. *The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment*. Oxford, UK: Elsevier Ltd.

Khor, C.S., Chachuat, B. & Shah, N., 2014. Optimisation of Water Network Synthsis for Single-Site and Continuous Procesesses: Milestones, Challenges and Future Direction. *Industrial & Engineering Chemistry Research*, 53, pp.10257-75.

CHAPTER 6

Conclusion

In this work, the synthesis of optimal integrated water networks, where water using operations and water treatment operations are combined into a single water-regeneration network for the minimisation of freshwater intake and wastewater generation was addressed. By means of a process integration framework, the problem was approached using mathematical programming techniques that can systematically capture the full details of the system into models.

The norm when tackling these problems has been to represent regenerators using oversimplified relations that may potentially lead to inaccurate cost representations and consequently forfeit the objective of the investigation. In view of this shortcoming, this work incorporated detailed regenerator models within the water network model such that water network synthesis is achieved simultaneously with the regenerator design. In this way, water is not saved at the expense of regeneration energy since these variables are translated into monetary terms and optimised simultaneously. The regeneration technology chosen for this study is electrodialysis.

To demonstrate the applicability of the model that was developed, it was applied to a pulp and paper literature case study. Different scenarios were studied and compared using this case study. The results showed that with detailed regenerator models that have flexible performances, minimum economic and water targets can be achieved alongside optimum design specifications for the treatment units. This allows for better control of the system. Savings of up to 13% in freshwater intake, reduction of up to

16% in wastewater generation and a 14% saving in the total annualised cost can be achieved.

Owing to the structure of the problem modelled as an MINLP, there were drawbacks in terms of large computational time. This need not be a major setback since the problem is a design problem that is solved once off with no requirement for repetitive program executions such as is experienced in scheduling. Nonetheless, recommendations on how to improve the computational time as well as ways in which the model could be enhanced on a practical point of view were suggested.

Overall, incorporation of detailed regenerator models is beneficial since it allows for a complete detailed analysis of the system without any disregard to important factors such as energy. In this way the optimisation of such water networks for minimum water targets becomes a powerful and sustainable water management tool that can be valuable both to industry and the environment at large.