



Optimization of Integrated Water and Multiregenerator Membrane Systems

by

Musah Abass (920978)

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Supervisor: Prof. Thokozani Majozi

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Synopsis

Water and energy are key resources in the process industry. The water-energy nexus considers the interdependence of water and energy resources and their effect on the environment. The increasing awareness of environmental regulations has heightened the need for process integration techniques that are environmentally benign and economically feasible. Process integration techniques within water network synthesis require a holistic approach for the sustainable use of water through reuse and recycle and regeneration reuse and recycle.

Conventional methods for water minimisation through water network synthesis often use the “black-box” approach to represent the performance of the regenerators. The degree of contaminant removal and cost of regeneration are represented by linear functions. This, therefore, leads to suboptimal operating conditions and inaccurate cost representation of the regeneration units.

This work proposes a robust water network superstructure optimisation approach for the synthesis of a multi-regenerator network for the simultaneous minimisation of water and energy. Two types of membrane regenerators are considered for this work, namely, electrodialysis and reverse osmosis. Detailed models of the regeneration units are embedded into the water network superstructure optimisation model to simultaneously minimise water, energy, operating and capital costs. The presence of continuous and integer variables, as well as nonlinear constraints renders the problem a mixed integer nonlinear program (MINLP). The developed model is applied to two illustrative examples involving a single contaminant and multiple contaminants and one industrial case study of a power utility plant involving a single contaminant to demonstrate its applicability. The application of the model to the single contaminant illustrative example lead to a 43.7% freshwater reduction, 50.9% decrease in wastewater generation and 46% savings in total water network cost. The multi-contaminant illustrative example showed 11.6% freshwater savings, 15.3% wastewater reduction, 57.3% savings in regeneration and energy cost compared to the water network superstructure with “black-box” regeneration model. The industrial case study showed a savings of up to 18.7% freshwater consumption, 82.4% wastewater reduction and up to 17% savings on total water network cost.

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CHAPTER 1

INTRODUCTION

1.1 Background

Water and energy are key components in the process industry, and great amounts of each resource are consumed to produce the other. This inherent interdependence of water and energy is known as the water-energy-nexus (Desai, 2013). The water-energy nexus considers the interdependence of water and energy resources and its holistic effect on the environment. The increasing demand on water and energy resources coupled with stringent environmental regulations on effluent discharge limits has heightened the need for sustainable use of both water and energy resources. Sustainable use of water and energy, together with environmental regulations, present challenges which require effective process integration techniques.

Process integration is often employed in order to achieve a holistic water network superstructure for water and energy minimisation (El-Halwagi, 1997). This is done through an integrated water network that is open for direct reuse and recycle and regeneration reuse and recycle for sustainable use of water and energy. Insight-based and mathematical based optimization techniques are the two main approaches adopted in addressing water network synthesis. The insight-based techniques use water pinch analysis which does not require computational algorithms in generating solutions. A mathematical model is usually formulated based on a superstructure. A superstructure represents a superset of all feasible solutions to the problem. Mathematical optimization techniques allow the treatment of water network synthesis problems in their full complexity by

considering representative cost functions, multiple contaminants, and various physical and economic constraints (Takama, et al., 1980, Gunaratman, et al., 2005).

Membrane systems for water purification have often been used as regeneration systems within WNS. The purification of water through membrane systems is an energy intensive process and is directly associated with the capital and operational cost (Tsiakis & Papageorgiou, 2005). There is, therefore, a trade-off between water minimization and cost of regeneration. Earlier efforts concentrated on the design and synthesis of the stand-alone regeneration subnetwork in a distributed water network where the aim was to provide a certain amount of portable water to satisfy certain demands (Galan & Grossmann, 1998). In most published works, membrane systems have been represented using the “black-box” approach which uses a removal efficiency and linear cost functions (Tan, et al., 2009; Yang, et al., 2014). This approach does not, however, give an accurate cost representation of the membrane systems. There is, therefore, a need for a technique that would cater for energy minimization through a detailed synthesis of membrane regeneration systems in order to obtain optimal variables that affect the operation and economics of the regenerator unit.

Thus far, most work on water network regeneration and synthesis has not considered simultaneous water and energy minimization within a water network superstructure. In addition, there has been no published work that focuses on the integration of detailed multi-membrane regeneration units within a water network for the simultaneous minimization of water and energy.

The aim of the research presented in this thesis is to develop a systematic technique that would simultaneously optimize energy and water consumption within a water network superstructure (WNS). The technique is based on an integrated water and membrane-regeneration network superstructure. The membrane regenerators are Electrodialysis (ED) and Reverse Osmosis (RO) for partial purification of effluent for reuse and recycle. A detailed synthesis of the membrane regeneration systems is conducted to determine optimal operating conditions for efficient energy usage and also to give a true cost representation as

compared to the “black-box” method in terms of costs. The detailed model of the regenerators is incorporated in the overall water network objective function in order to minimize water and energy consumption as well as capital and operating cost.

The formulated model is applied to two illustrative examples and one industrial case study to demonstrate its applicability in simultaneous water and energy minimization. The first illustrative example involves effluent with single contaminants, whereas the second illustrative example involves effluent with multiple contaminants. The ED model in this work can only remove single ionic contaminants. Therefore sequence specific constraints are introduced such that the ED unit caters for ionic contaminants within a stream involving multiple contaminants. The RO unit, however, is allowed to cater for both ionic and non-ionic contaminants within the multiple contaminants framework. The third case study which involves a power utility plant in South Africa considers effluent with single contaminants. Contrary to what is commonly practiced in literature, the removal ratio in this work is presented as a variable. This is done to give the model an additional degree of freedom for better performance of the regeneration units. The overall water network problem is formulated as a mixed inter nonlinear program (MINLP) and solved in GAMS. The general purpose global optimization solver BARON, which uses the branch-and-reduce algorithm (Tawarmalani and Sahinidis, 2005) to obtain a solution, was used. The model was run using a 64 Bit version of Windows 7 Professional on an HP desktop computer with Intel® Core (TM) i7-4770 processor 3.40 GHz and 8.00GB of RAM.

1.2 Motivation

Within the realm of process water management, regeneration reuse and recycle have been used as a means for water minimization. The motivation of this study is drawn from the work of Kuo and Smith (1998b). They developed a method to explore regeneration opportunities within a water network based on three steps: Pinch identification, operation grouping, and operation migration. Their

methodology was applied to a case study adopted from Wang and Smith (1994a). The first step in Kuo and Smith (1998b) procedure is pinch identification, where a water supply line is used to identify pinch concentration as shown in Figure 1.1. After pinch identification, Kuo and Smith (1998b) divided the operations into two groups. The first group (Group I) is operations below pinch which need freshwater and the second group (Group II) is operations on or above pinch that can use water from other operations or regeneration units as shown in Figure 1.1. The operation migration mechanism is then conducted to explore possible improvements to the water network.

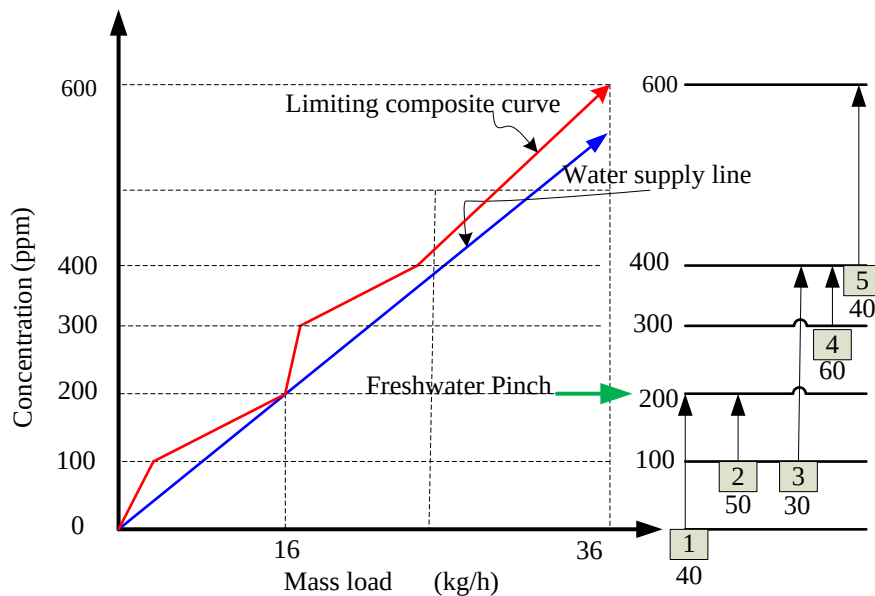


Figure 1.1: *Pinch identification and operation grouping (Kuo & Smith, 1998b)*

Kuo and Smith (1998b) used two mechanisms; the first mechanism is a migration of operations below water pinch from Group I to Group II in order to reduce the freshwater demand. The second mechanism is the migration of operations which are above freshwater pinch and below or across the regeneration pinch from Group II to I in order to reduce regeneration or freshwater target as shown in Figure 1.2.

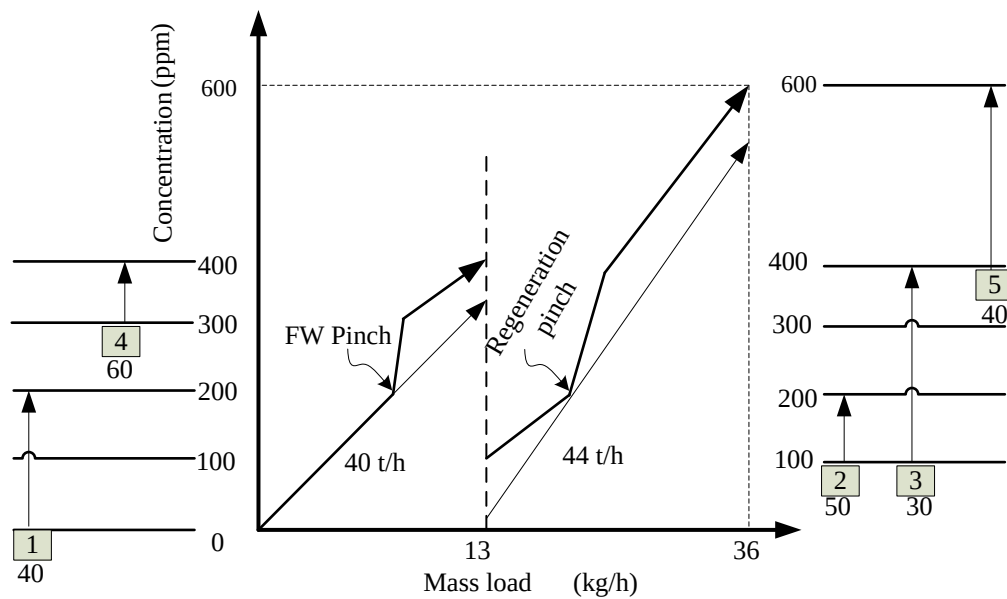


Figure 1.2: *Using mechanism I and II to achieve targets (Kuo & Smith, 1998b)*

Kuo and Smith (1998b) achieved a reduction in the freshwater target from 80 t/h in the work of Wang and Smith (1994a) to 44 t/h through regeneration reuse. The resultant optimal water network design is presented in Figure 1.3.

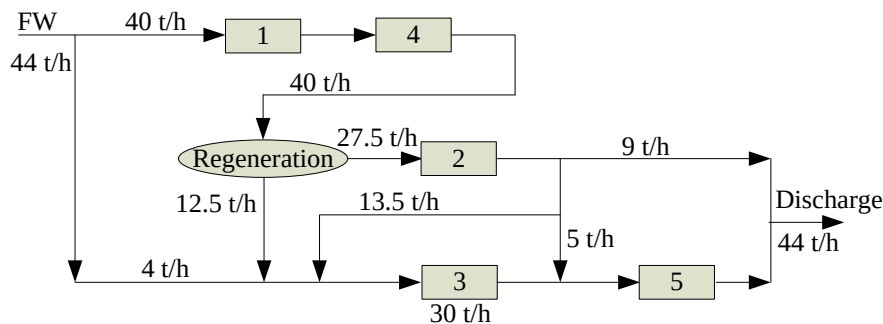


Figure 1.3: *Optimal design for regeneration reuse (Kuo & Smith, 1998b)*

Kuo and Smith (1998b) applied the same procedures to further reduce water demand through regeneration recycle within a water network from 80 t/h in the work of Wang and Smith (1994a) to 40 t/h.

The work of Kuo and Smith (1998b) achieved freshwater savings of 45% and 50% through regeneration reuse and recycle. The capital and operational cost of the regeneration units, as well as the overall water network was however, not taken into consideration. They also characterized the regeneration units by a fixed

removal ratio which does not give regeneration units the degree of freedom to improve their performance. Characterizing regeneration units by their removal ratio results in a misrepresentation of the unit design requirements, as different regeneration units perform differently depending on the amount and type of contaminants to be removed, the flow through the unit, the regeneration unit efficiency as well as the configuration of the regeneration unit.

The current work, therefore, seeks to simultaneously optimize energy and water within a water network taking into account regeneration reuse and recycle as well as operation and capital cost of the overall water network. The removal ratios of the regeneration units are set as variables. Variable removal ratios give the regeneration units the degree of freedom to explore their potentials.

1.3 Objectives

The objectives of this study can be summed up as follows:

- To develop a complete WNS with multiple membrane partitioning regenerators that is open to parallel and series connections and reuse and recycle within the WNS.
- To develop a mathematical model based on the WNS incorporating detailed models of the regenerators in order to minimize water and energy consumption.
- To determine the optimal operating conditions of the regeneration units.
- To explore the idea of using a variable RR (removal ratio) to describe the performance of the regenerators.
- To validate the model with a literature study in order to show the practicality of the model.

The basis for this work is to demonstrate the importance of water regeneration with a detailed model of the regeneration units against the commonly practiced “black-box” model within a water network superstructure optimization framework.

The problem statement in this work can be stated as follows:

Given:

- (i) A set of water sources, J , with known flowrates and known contaminant concentrations that are amenable for reuse/recycle.
- (ii) A set of water sink, I , with known flowrates and known maximum allowable contaminant concentration.
- (iii) A set of membrane regeneration units with the potential for parallel and series connections for partial treatment of wastewater from sources for reuse and recycle.
- (iv) A freshwater source, FW , with known concentration and variable and unlimited flowrate.
- (v) A wastewater sink, WW , with maximum allowable contaminant concentration and variable and unlimited flowrate.

Determine:

- (i) The minimum freshwater intake, wastewater generation, the energy consumed in the ED and RO units, and the total annualised costs for ED and RO.
- (ii) Optimal water network configuration.
- (iii) Optimal design variables of the regenerators.

1.4 Thesis Structure

The rest of the thesis is divided into the following chapters:

- i) Chapter 2 provides a comprehensive review of the literature focusing on both graphical and mathematical methods for water network synthesis and optimisation. A literature review is also presented on the different membrane systems and approaches for water minimisation in water network frameworks together with different mathematical optimization techniques.

- ii) Chapter 3 presents a detailed model development of the study. This includes detailed models of both membrane regeneration units. The developed model is a comprehensive model that can cater for single and multiple contaminants framework.
- iii) Chapter 4 shows the validation of the developed mathematical model against illustrative example obtained from literature.
- iv) Chapter 5 presents the application of the developed mathematical model in Chapter 3 to a real life industrial case study involving a power utility plant.
- v) Chapter 6 provides limitations of the developed model and recommendations for future work drawn from the study.
- vi) Chapter 7 presents the summary of the work presented.

1.5 References

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This section gives a detailed literature review of previously employed process integration techniques for water network synthesis (WNS) and optimization in this area of research. The section starts with a general and comprehensive review of WNS and optimization methods. This includes characteristics of water networks, water minimization approaches, as well as analysis of both graphical and mathematical optimization techniques within WNS. This is then followed by an extensive review of membrane filtration technology with particular interest on electrodialysis and reverse osmosis. The chapter concludes with discussion of the strengths and limitations of water network optimization techniques based on non-convexity, nonlinearity, and uncertainty.

2.2 Water Networks Synthesis

Process synthesis is the distinct decision making of determining the number of available components to be used and how they should be interconnected to obtain optimal solution of a design problem (El-Halwagi, 1997). The minimization of water in the process industry can be achieved by optimization of water networks using process integration and synthesis techniques. A water network synthesis (WNS) is the design, synthesis and retrofit of water network for both batch and continuous operations (Khor, et al., 2014).

Water minimization is the reduction of freshwater consumption and wastewater generation within a water network (WN) in a process unit. A water network is a collection of water using processes that uses or produces water, and operations that treat or regenerate effluents (Jezowski, 2010). Freshwater sources, wastewater disposal sites, mixers splitters, and storage tanks may include some of the elements of a WN. Depending on the size of a problem, water network synthesis may involve water-using units or wastewater treatment operations or both (Khor, et al., 2014). Water-using processes or process units consist of both water sources and water sinks. Water sources are process units which generate streams that can be utilized for reuse/recycle, regeneration or discharged as waste. A water sink on the other hand is process unit which consume water from sources, freshwater sources and regeneration units.

2.2.1 Water Network Characteristics

Water-using networks (WUN) are water networks that consist of sources and sinks within the water network. When a regeneration unit is included in a water network for partial treatment of effluent to enhance its quality for reuse/recycle, it becomes a water regeneration networks system (WRNS). When an end-of-pipe effluent treatment is added to the water network unit it becomes total water network synthesis (TWNS) this is described in detail later in the chapter. A combination of regeneration units with TWNS gives rises to a complete water system synthesis (CWSS)

Water using processes can be further classified into mass and non-mass transfer processes. Within water network optimisation fixed mass load operations also known as quality controlled operations can be classified as the preferential transfer of species from a highly contaminated stream to water. The lean stream (water), which is usually referred to as the *mass separating agent* (MSA) These types of operations are usually carried out in solvent extraction, absorption and equipment washing (Jezowski, 2010; Poplewski, et al., 2011; Manan, et al., 2004). In mass transfer-based water operations water is fed into the vessel as demanded and wastewater is generated as source (Figure 2.1a), or it can be used in an

absorption process where water as a mass separating agent (MSA) is used to remove contaminants as represented in Figure 2.1b.

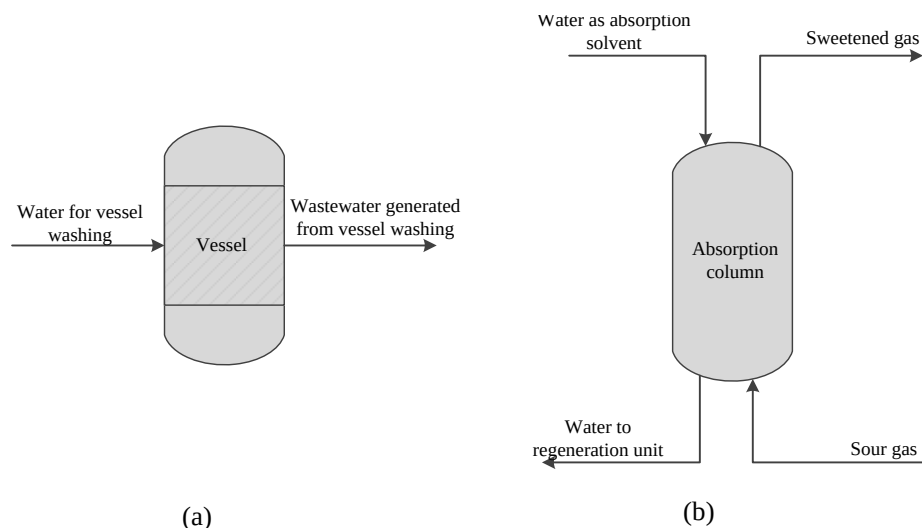


Figure 2.1: Mass transfer-based water using operations (Manan et al., 2001)

Non-mass transfer-based or quantity controlled methods relates to functions of water rather than it being a MSA. Water in non-mass transfer-based operations is used as a raw material being fed into a reactor or being withdrawn as an end product in a chemical reaction. This is illustrated in Figure 2.2.

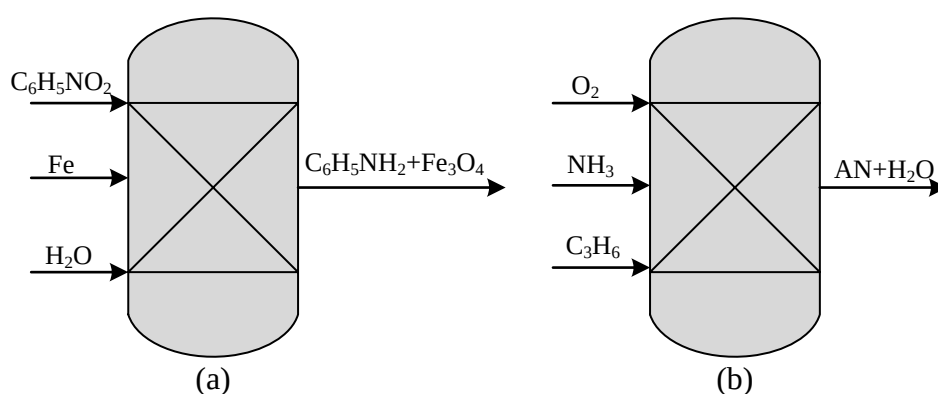


Figure 2.2: Non-mass transfer-based water-using operations (Manan, et al., 2004)

2.2.2 Water Management Approaches

Water network synthesis for water recovery can be grouped into four categories as adopted in Wang & Smith, (1994a,). These are illustrated in Figure 2.3a to Figure 2.3d.

Direct water reuse. Figure 2.3a shows a direct water reuse network. This process allows water to be directly reused in other processes where the contaminant levels of water are within the process limits. In a water reuse network water can be blended with other wastewater from other processes or freshwater in order to lower the contaminant levels before being sent to other processes (Wang & Smith, 1994b).

Direct water recycles. This entails reusing water in the same process unit where it was produced, as shown in Figure 2.3b. In direct recycle, wastewater from processes is not partially treated to enhance its recycle potential. Freshwater is usually added to wastewater from processes in order to lower contaminant levels for it to be recycled. Direct recycle system of water network is not an economical way of water minimization as it demands more freshwater for it to be functional and there is also a high risk of contaminant accumulation in process units.

Regeneration reuse. AS shown in Figure 2.3c effluents from sources are partially treated to enhance its quality in order to be reused in other processes. Water from processes in a regeneration reuse water network does not go back to previous processes where it was generated or previously being used. Applications of regeneration reuse are solely practiced in order to prevent accumulation of harmful contaminants in process units where the streams were previously generated.

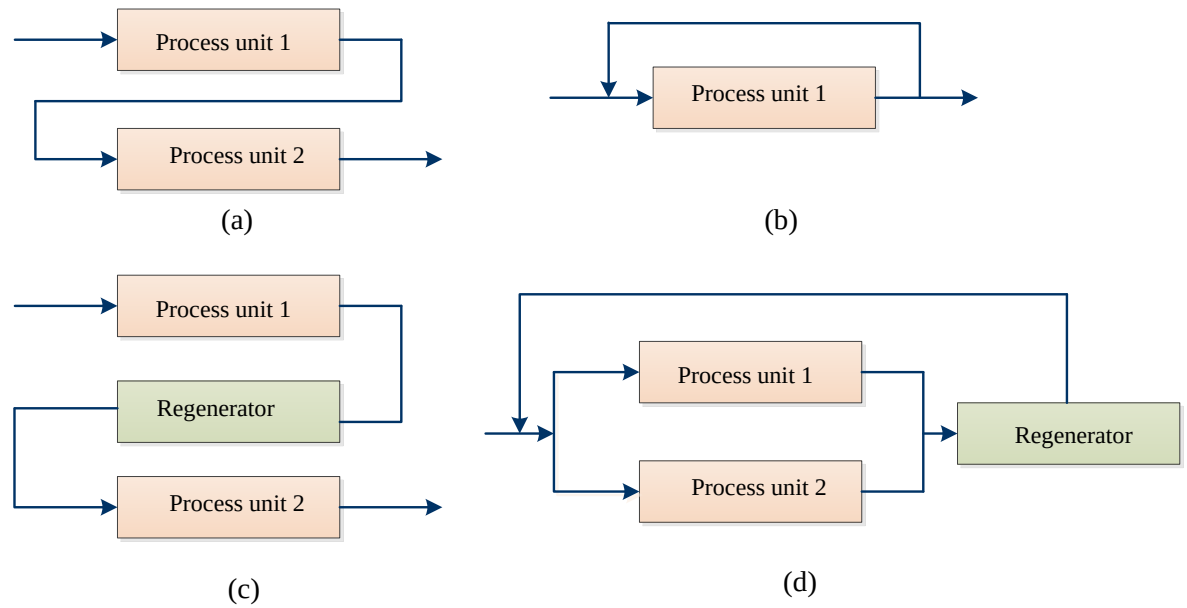


Figure 2.3: Water minimization schemes

Regeneration recycle. As shown in Figure 2.3d, water from the source is partially treated and recycled in process units where it was generated. Although applications of regeneration recycle are novel, previous efforts have always focused on minimization of freshwater intake allowing multiple streams to be recycled (Sienutycz & Jezowski, 2009). There were no environmental considerations for final contaminant concentration of effluents. However recent efforts have included waste sinks for final treatment of wastewater to meet environmental discharge limits.

It is important to have a water network that includes all the above schemes, which can be optimized to guarantee alternative water reuse, regeneration reuse/recycle minimization of cost and meeting of environmental effluent discharge limits. Such a scheme is called water regeneration network synthesis (WRNS).

2.2.3 Total Water Network

Apart from the four water minimization schemes discussed above, other water network synthesis for water minimization have been discussed in literature as follows. Figure 2.4 is a schematic of a total water network, which comprises water

using units such as the sources, sinks and effluent treatment systems (ETS) which treats water to the discharge quality. Because of complexity of total water network design problems, most research often focused on two separate sub-networks called water using networks (WUN) and wastewater treatment network (WWTN) (Poplewski, et al., 2011). Water using networks (WUN) do not usually take regeneration into consideration. And wastewater reuse is the only avenue to reduce freshwater consumption. However recent approaches on wastewater minimization by water using networks (WUN) have focused on the use of regeneration units to minimize freshwater consumption and consideration are not made on discharge limit concentration (Poplewski, et al., 2011).

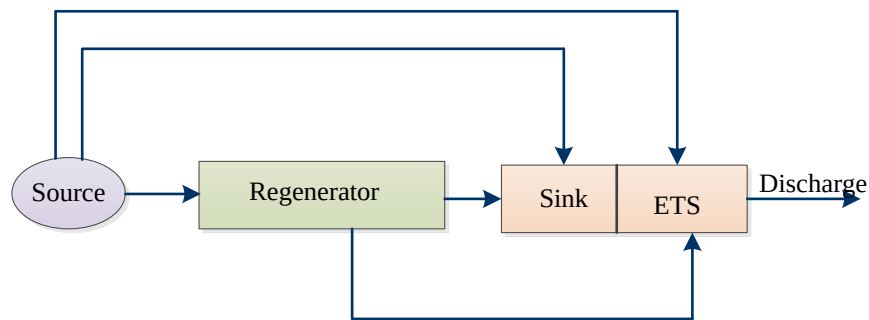


Figure 2.4: Schematic of a total water network (Khor, et al., 2014)

It is possible to achieve a close circuit of process water by designing a total water network (TWN), where discharge of effluent to the environment can be eliminated. Freshwater is used as make-up water. This practice is expensive because more freshwater is consumed and also solid deposits accumulate in process units (Bagajewicz, 2000).

2.2.4 Central Water Treatment Network

Conventionally, wastewater generated in processes has been treated in central treatment facilities in order to meet environmental disposal limits.

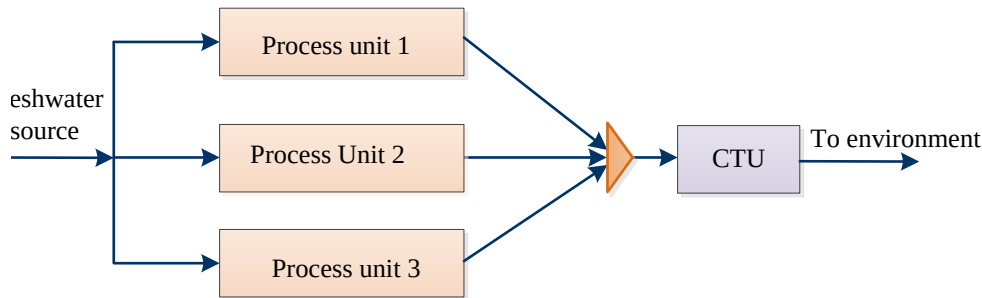


Figure 2.5: Central water treatment network (Sienutycz & Jezowski, 2009)

In a centralized wastewater treatment facility (Figure 2.5) all effluent streams are mixed in a central treatment unit which often leads to large volumes of wastewater with low concentrations of contaminants (Wang & Smith, 1994b; Shi & Liu, 2011). In centralized effluent treatment systems, combining waste streams that require different treatment technologies results in combined costs of treating all streams and it is always more expensive than treating separate streams individually (Wang & Smith, 1994b). However, if two waste streams require the same treatment technology, then it is economically feasible to combine both streams for treatment.

A water network of central treatment unit arrangement requires a large amount of freshwater and since there is no provision for water reuse/recycle, it generates a high quantity of wastewater to be treated (Sienutycz & Jezowski, 2009). This results in high investment and operating costs. According to McLaughlin et al. (1992), wastewater treatment operations costs are proportional to the total flow rate of the effluent. Hence the cost of effluent treatment increases with decreasing contaminant concentration for a given mass load of contaminant in a central treatment unit (Shi & Liu, 2011). It is therefore economically effective to design effluent treatment systems that are capable of separating waste streams for treatment and only combine them when it is appropriate. When this objective is met, centralized effluent treatment systems become distributed effluent treatment systems (Eckenfelder, et al., 1985; Lankford, et al., 1988; Higgins, 1989; Wang & Smith, 1994b). Distributed effluent treatment systems lead to a significantly lower

capital and operating costs compared to centralized effluent treatment systems (Wang & Smith, 1994b).

2.2.5 Distributed Water Treatment Methods

Unlike the centralized wastewater treatment network, distributed wastewater treatment network consist of mixing and bypassing scheme as displayed in Figure 2.6.

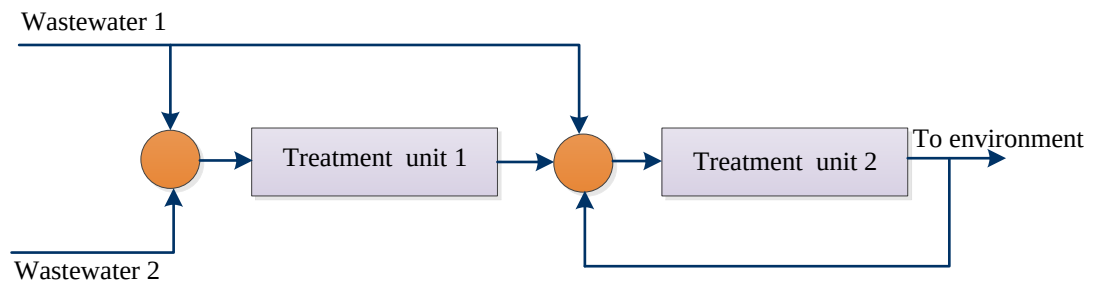


Figure 2.6: Distributed wastewater treatment network (Sienutycz & Jezowski, 2009)

This type of treatment system calls for streams to either be partially mixed, or separately treated in order to reduce effluent flowrate through the treatment system (Sienutycz & Jezowski, 2009). The main objective of such a system is to minimize wastewater flow rate in order to minimize wastewater treatment cost.

Water allocation planning (WAP) is another water minimization concept within the water network optimization framework. WAP is based on the principle of water reuse and recycle to minimize freshwater consumption and wastewater generation with the aim of adequately allocating water to processes in terms of quality and quantity (Bagajewicz & Savelski, 2001). The combination of a distributed water network system with WAP results in WRNS. The regeneration in this instance can be any water treatment technology, ranging from membrane systems, non-membrane systems for water treatment. The incorporation of the regeneration units becomes essential when the cost of freshwater is higher than the cost regeneration. It is therefore essential to conduct accurate cost

considerations in terms of energy and capital cost of the regeneration unit within a water network optimization framework. Different approaches have been used over the years and the very important and major ones are discussed in the next section.

2.3 Methods for Water Network Synthesis and Optimization

Various efforts have been made using different kinds of methods on the synthesis of water networks involving reuse/recycle, regeneration reuse/recycle. Within the realm of process optimization for water minimization, the methods for water minimization design and targeting, can be identified and grouped into two main categories: the water pinch techniques and the mathematical-based optimization approaches.

2.3.1 Pinch or Graphical-Based Optimization Efforts

Pinch technology is a process integration technique which was initially developed by Linnhoff & Hindmarsh, (1983) for heat recovery in heat exchanger networks (HENs) using thermodynamic principles. They achieved the highest degree of energy recovery at a minimal cost by developing optimal HEN based on the location of pinch points. El-Halwagi & Manousiouthakis (1990) later extended the concept to mass exchanging network (MENs) processes. They used the technique to enhance the configurations of MENs to maximise the amount of species to be transferred from a rich stream to a lean stream in a network.

Wang & Smith (1994a) later extended the pinch technology by proposing the seminal graphical method which sets to target water minimization. They used the concept of water composite curve which they termed the limiting water profile to achieve optimal freshwater required in a system. This is represented in Figure 2.7, where the relationship between concentration and impurity load for rich stream and water profile is shown. This concept starts by developing limiting water profiles for each unit operation where each profile depicts the limiting case when minimum water flowrates is used by a unit. This is the situation when the maximum inlet and outlet concentrations of the wash streams are specified.

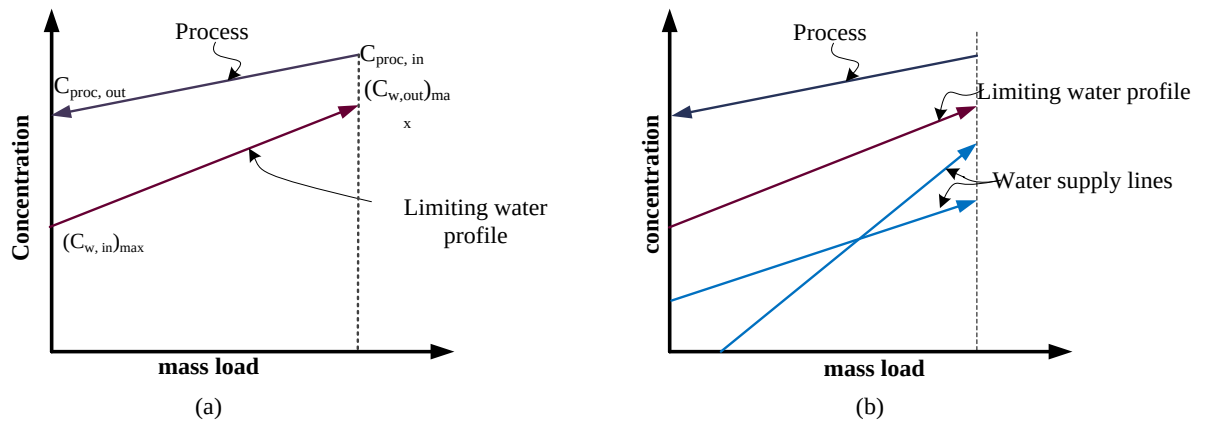


Figure 2.7: Limiting composite curves for limiting water profiles

Individual profiles can be combined to form a limiting composite curve for all water using processes. This will include the sources and the sinks with their corresponding flowrates and concentrations within the plant. The minimum water flowrate target is achieved by matching the overall supply line against the limiting composite curve as shown in Figure 2.9. The steepest point of intersection between the supply line and the composite curve is known as the *pinch point*. Based on Figure 2.8, operations below the pinch point requires more freshwater and those above pinch can reuse water in other operations. Wang & Smith (1994a) also maintains that operations under the pinch point needs to be considered for further water minimization through reuse/recycle and regeneration reuse/recycle. After attaining the minimal water target, rules are employed to design the set of alternative network structures where each is evaluated for its practical applicability and the best design chosen.

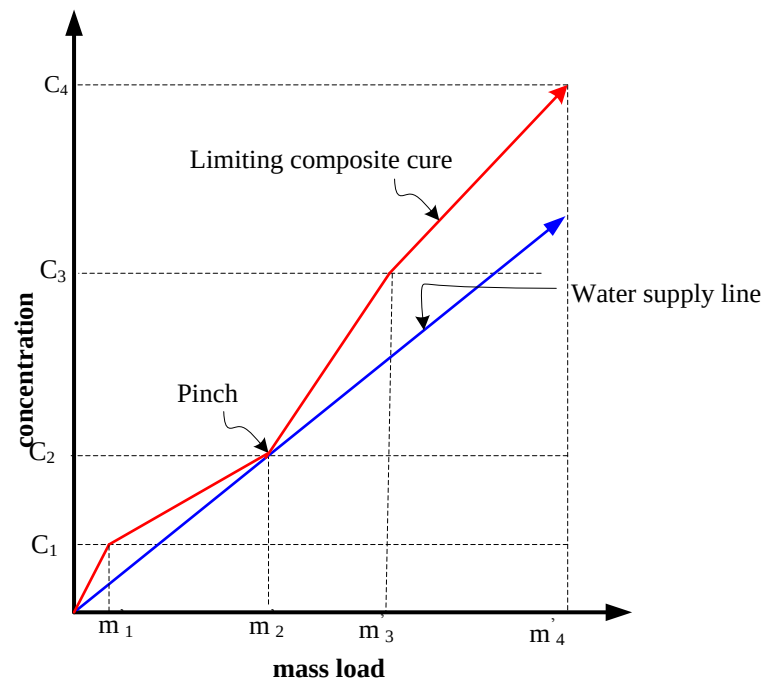


Figure 2.8: *Limiting composite curve for minimum water flowrate at pinch point*

Wang and Smith (1994b) proposed important insights into the design of distributed effluent treatment systems in terms of streams to be fully treated, partially treated and streams that should partially bypass treatment units based on their position to pinch point. The method also gave in-depth information for costs to be allocated to the water network and allow for all possible options to be explored and optimized. They later extended the idea to situations where flowrates are constrained. However, the proposed method failed to give the best targets in some cases when the pinch for the problem shifts to a different position. The work was also limited to mass transfer-operations hence water used as cooling and heating media in cooling towers, boilers and reactants could not be properly represented. Application of the method was also very difficult with respect to problems involving multi-contaminant streams. Mainly because single construction was used to represent the treatment system before and after regeneration, hence, multiple contaminant problems render the profile of the contaminant to change completely. Some operations needed to split in order to achieve targets, which complicates the design and usually not feasible, requiring an increase in water

consumption in order to remove the split. The regeneration potential was not fully explored in terms of taking into account the impact of effluent treatment.

Kuo & Smith, (1997) provided an extended insight into the work of Wang & Smith, (1994a,b), where effluent treatment flowrate was targeted and distribution of load between multiple treatment processes was addressed. They used a graphical representation for targeting regeneration units, which overcame the challenges of the seminal work of Wang and Smith (1994a) and details into trade-offs between water minimization and effluent treatment units. The work of Kuo & Smith (1997) also focused on wastewater degradation to account for the rate of contaminant treatment in cases of multiple contaminants and treatment units. However, their method called for the design of multiple subsystems to calculate rate of degradation of the wastewater, which demanded unrealistic efforts, especially in larger systems.

In a later development Kuo & Smith, (1998a) developed a much simpler method base on hypothetical *water mains* which act as sources and sinks depending on their position. They used a four step design procedure to attain minimum water targets and create favorable wastewater streams for treatment. Figure 2.9 presents the basis for the water network design which is outlined as follows:

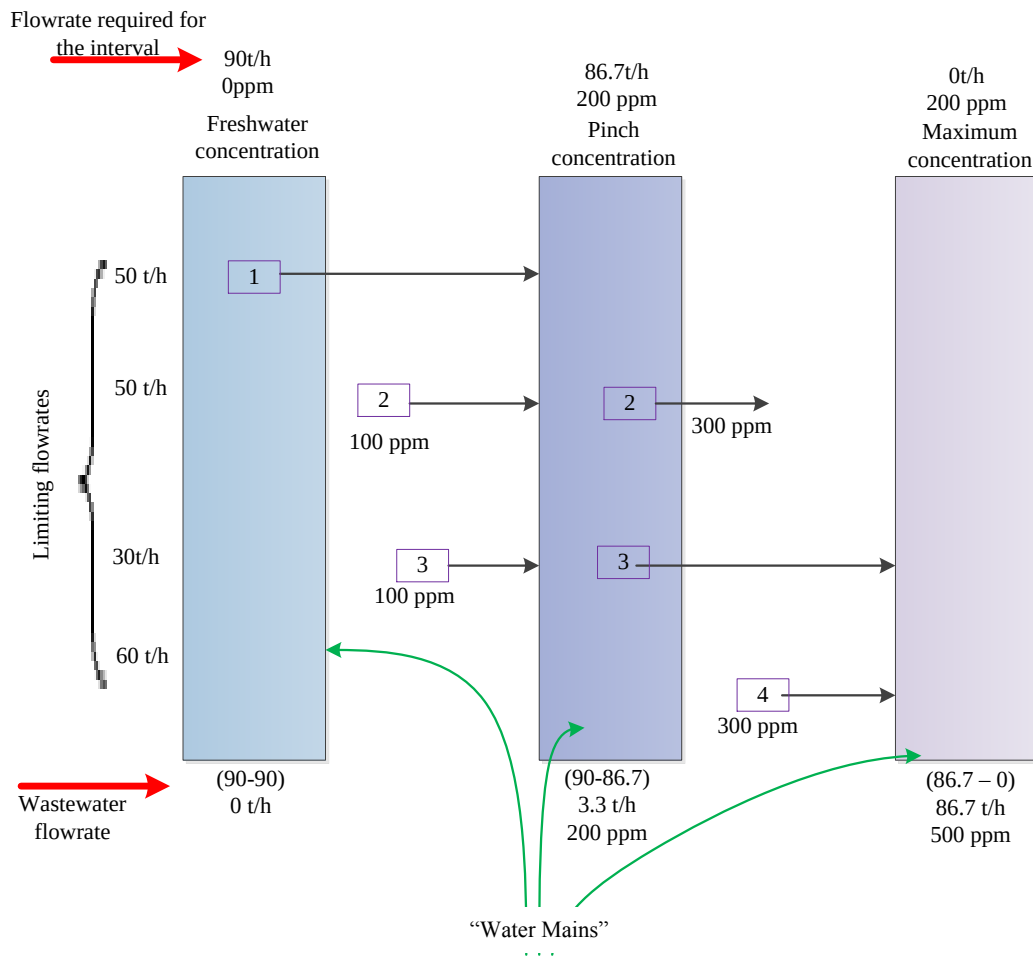


Figure 2.9: Design grid for water mains (Kuo & Smith, 1998a)

Step 1: Set up the grid design. A design grid is developed as can be illustrated in Figure 2.9, where three water mains are developed with corresponding freshwater concentrations, pinch concentrations, and maximum concentrations. The design grid also shows limiting flowrates and wastewater generated by each main.

Step 2: Connect operations with water mains. The second step requires operations to be connected with the water mains in order to meet the requirements of each operation.

Step 3: Merge operations crossing boundaries. The third step requires operations that cross the water main to be merged before the process begins. This is done to avoid operations that cross the water main as can be seen in 2 and 3 in Figure 2.10, to be represented as two separate operations. Such an overlap in operation

on the water main creates different flowrates which is difficult or impossible to implement practically.

Step 4: Remove the intermediate water mains. The intermediate water main provides design strategy and hence acts a source and sink. Provided the sources can connect to the sinks directly, and as long as supplying and required flowrates can be matched with process constraints such as piping layout etc. are considered the intermediate water mains can be removed. This is represented by Figure 2.10, with the resulting flow sheet illustrated in Figure 2.11.

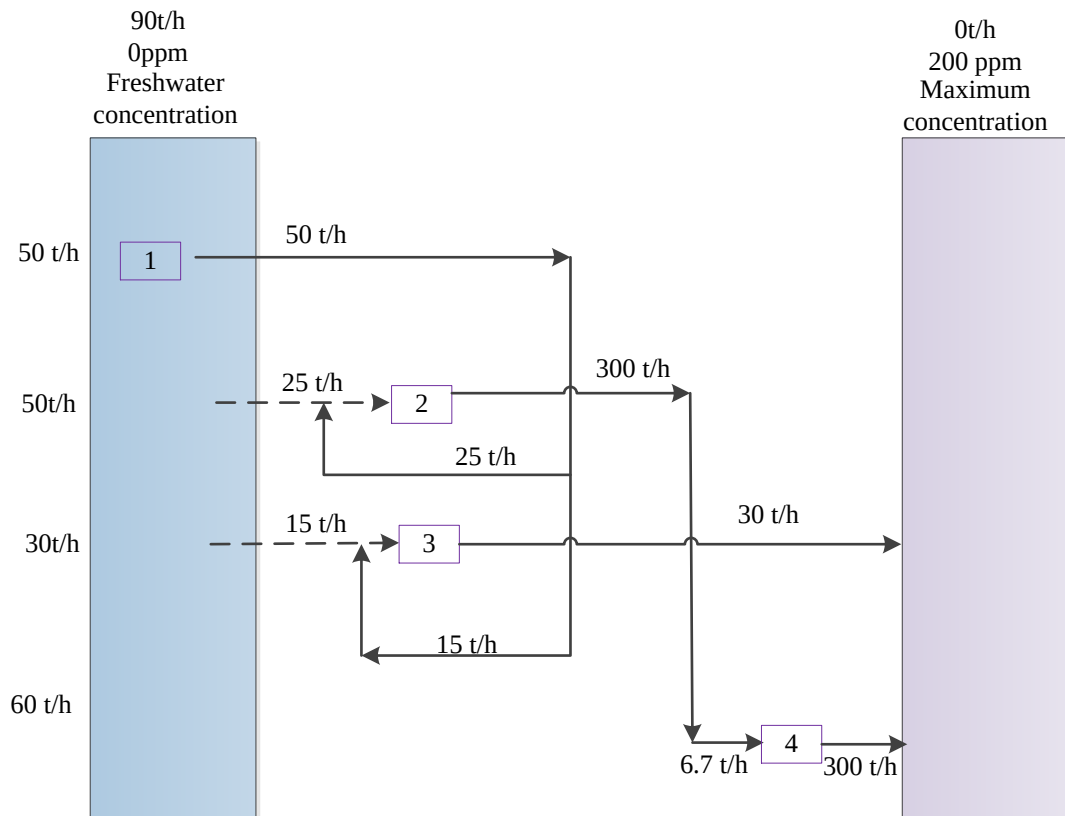


Figure 2.10: Design grid for the water network without water mains (Kuo & Smith, 1998a)

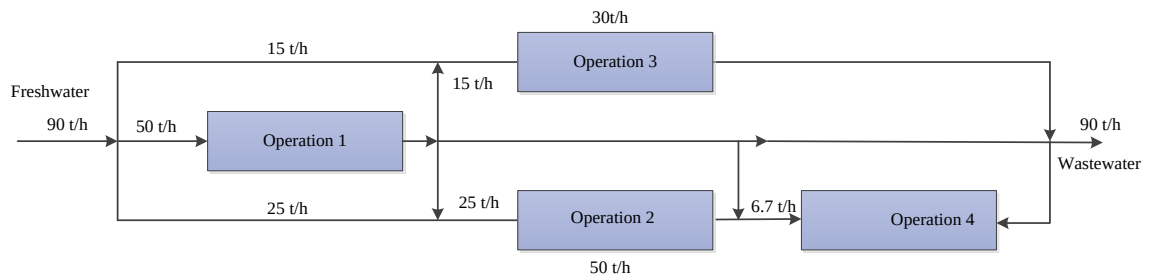


Figure 2.11: Final design flowsheet (Kuo & Smith, 1998a)

Kuo & Smith (1998b) introduced a new methodology to explore the regeneration opportunities within a water network superstructure. They incorporated regeneration units and effluent treatment units to cater for the difficulties encountered in previous works. Unlike the work of Wang & Smith (1994a), Kuo & Smith (1998b) divided streams into two groups, those that require freshwater and those that require regenerated water. They developed targets for freshwater, regeneration and number of treatment units, and streams were moved between the groups to refine targets. They argued that the methodology offers a better process configuration for regeneration units and the impact on effluent treatment units.

Dhole et al. (1996) identified similar drawbacks on the work of Wang & Smith (1994a). They argued that the mass transfer methodology could only cater for limited operations such as washing, extraction, scrubbing etc. and could not be applied to larger processes such as reactors, boilers, cooling towers etc. since the methodology focuses on flowrate and not the amount of contaminant concentrations. Dhole et al. (1996) also argued that the approach of Wang & Smith (1994a) could not cater for situations where several aqueous streams enter and leave a process unit at different concentrations. The model could not also cater for losses or gains of water as the flowrate through and out of a process.

Dhole et al. (1996) therefore presented an alternative method to cater for the limitations identified in Wang & Smith (1994a) work. They considered several contaminant concentrations through the inlet and outlet streams of a process with their respective concentrations. In their representation, Dhole et al. (1996)

developed a methodology that could handle operations that cannot be handled by mass transfer, dealing with operations with varying inlet and outlet contaminant concentrations, as identified in Wang & Smith (1994a).

Although the work of Dhole et al. (1996) is novel, it did have major setbacks, for example, pinch point and flowrate were dependent on an assumed mixing arrangement. Hence the methodology could not be considered to give a true targeting procedure. Polley & Polley, (2000) indicated that the apparent targets generated by Dhole et al. (1996), could lead to significantly higher than the real minimum freshwater and wastewater targets if the correct stream mixing technique was not identified. Sorin & Bédard, (1999) also identified the setbacks of the work of Dhole et al. (1996), they argued that the technique could not lead to several “local” pinch points which may not be true or global pinch points, hence they developed the *evolutionary table* to numerically determine the freshwater and wastewater targets.

Hallale (2002) pointed out that when more than one global pinch points occur in water using processes, the evolutionary table could not locate them properly. They therefore developed the *water surplus diagram* (WSD) to target minimum freshwater and wastewater. The water surplus diagram has similar characteristics to the water source demand composite curve proposed by Dhole et al. (2002). The method boasts a unique advantage over existing methods in terms of dealing with wider ranges of water-using processes, as well as representing convenient targets which are unique and not dependent on assumed mixing arrangements. Hallale (2002) used tedious iterative steps to construct the water surplus diagram which is illustrated in Figure 2.12.

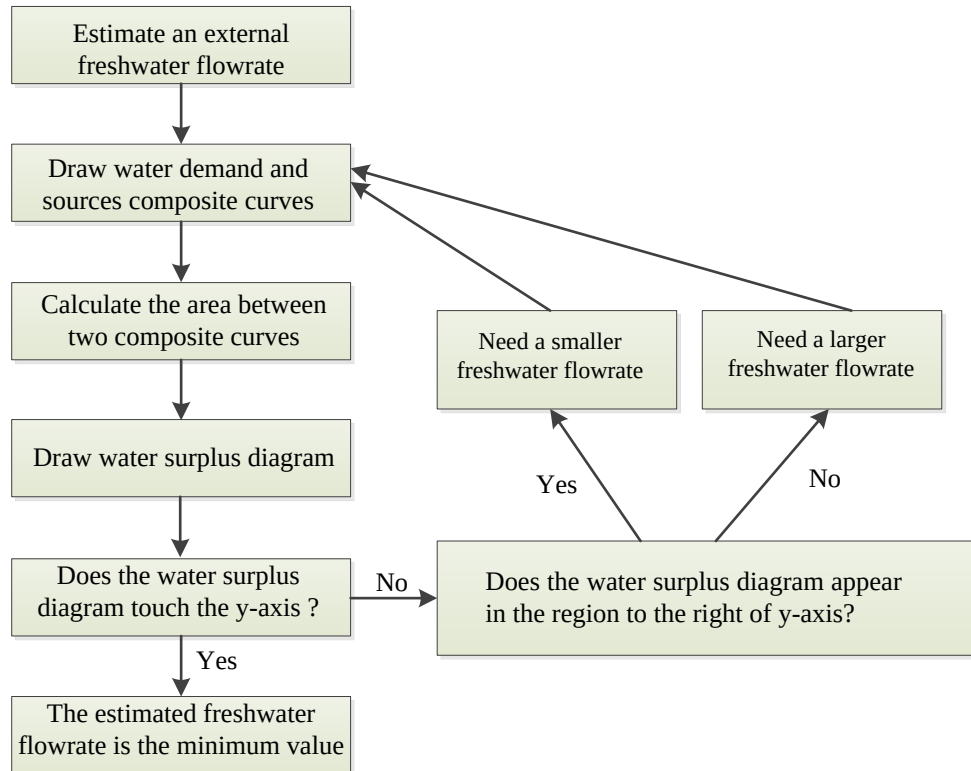


Figure 2.12: Iterative steps for constructing the water surplus diagram (Manan, et al., 2004)

The work automatically allows for all mixing possibilities to determine the accurate pinch point and reuse targets by giving targets a priori rather than a mere representation of a particular design. Based on the iterative procedure presented in Figure 2.12, a plot of a demand composite curve is done where the vertical axis shows the purity of water instead of contaminant concentrations, and the horizontal axis displays flowrates as shown in Figure 2.13.

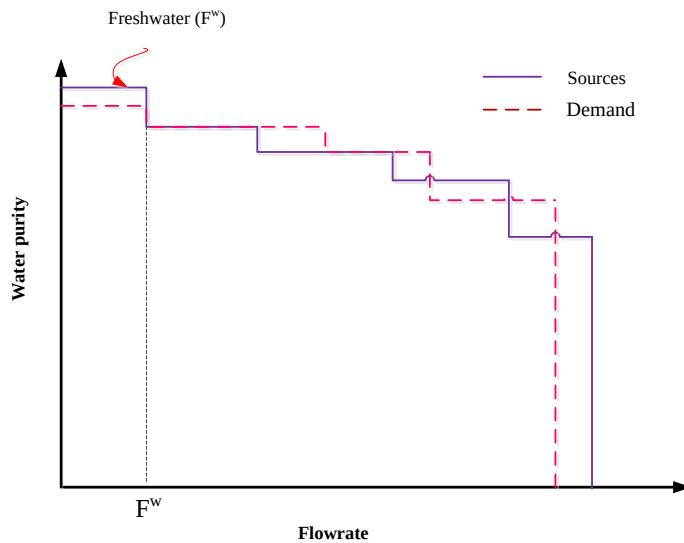


Figure 2.13: Construction of demand composite curve

An arbitrary freshwater value is assumed and included in the source composite. This is done to determine the true minimum flowrate which is unknown at the initial stage of the process. Water surplus diagrams are used to examine assume freshwater for feasibility. The water surplus diagram constructed will show regions where the source composite is either above or below the demand composite. This implies a surplus or deficient of pure water respectively. The area of the enclosed rectangles determines the pure water surplus and deficit. Figure 2.14 illustrates the water surplus diagram which is a construction of cumulative surplus verses the water purity.

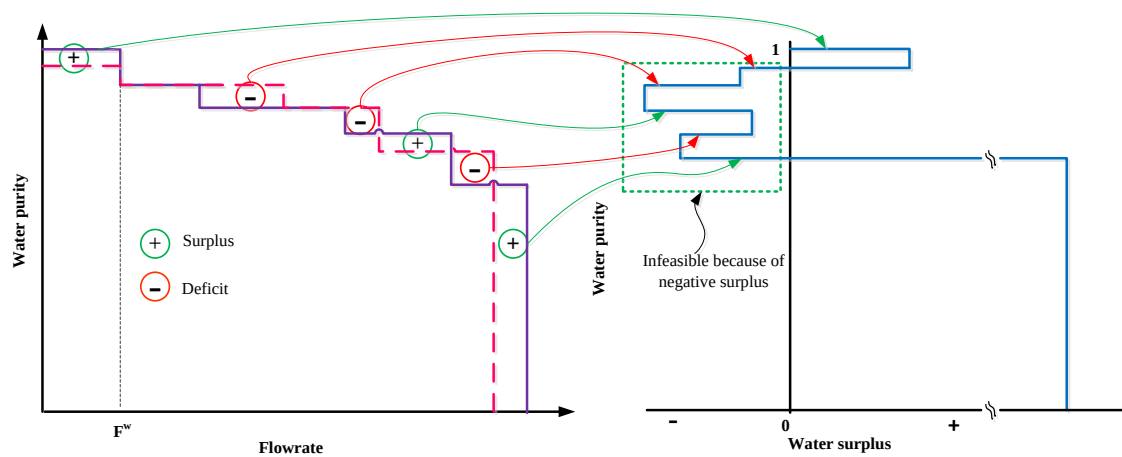


Figure 2.14: Construction of a water surplus diagram (Hallale, 2002)

The cumulative area is enclosed between the two composites which is an integral function, this automatically incorporates the possibility of mixing sources. With the assume value of freshwater flowrate, if part of the plot lies in the negative region, it means water purity will not be sufficient hence more freshwater is needed until no part of the surplus diagram is negative. The minimum freshwater and wastewater target is achieved when the procedure is repeated until the surplus diagram touches the vertical axis (Figure 2.15). The technique can be carried out by hand using a spreadsheet or computer code to avoid the tedious repetitive calculations.

The method of Hallale (2002), was not limited to mass-transfer-based operations and could therefore handle all mixing possibilities and still attain true pinch point and reuse target. The method however has the same drawbacks as composite curves, as it was tedious and time consuming to draw and also based on trial-and-error method to find pinch points and water targets.

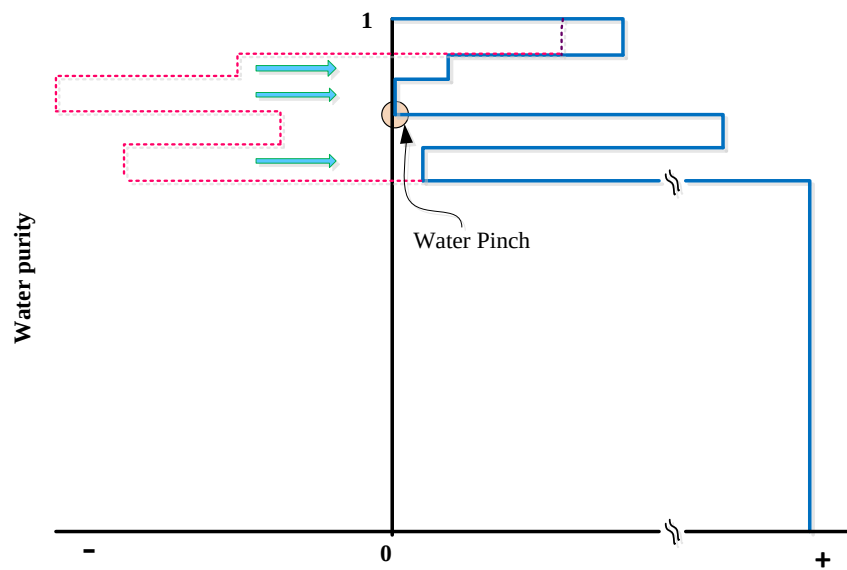


Figure 2.15: Determination of minimum water targets

Manan, et al. (2004) identified the drawbacks in the work of Hallale (2002), and presents the *water cascade analysis* (WCA) which is a new numerical technique to establish the minimum water and wastewater targets in a *maximum water recovery* (MWR) network. The WCA, just like the water surplus diagram is not limited to mass-transfer-based operations, and also eliminates hectic iterative steps to yield exact targets and pinch points.

Ng et al. (2007a,b) proposed graphical and algebraic approaches to identify waste streams in a total water network. The first part of the work proposes new targeting approach utilizing graphical approach by El-Halwagi et al. (2003) and Prakash & Shenoy (2005). They used a *material recovery pinch diagram* (MRPD) to identify flowrate targets of water for reuse/recycle in a water network. The graphical efforts provided conceptual understanding to problem synthesis, while the algebraic methods provide the flowrate targets. They addressed the interaction between waste treatment and water regeneration, and proposed that suitable selection of waste streams for regeneration or waste treatment will lead to minimum contaminant concentration load to be regenerated or treated in a waste

treatment unit. This will lead to a total reduction in water treatment network capital and operations cost.

Foo (2009) presented a state-of-the-art review of previous graphical pinch-based techniques developed in the 21st century. The focus of the work was on single contaminant with fixed flowrates. Comparisons were developed between the present techniques and the single contaminant fixed flowrates problems, and also with problems that have been addressed with respect to fixed load problems. Foo (2009) recommended that future research efforts should focus on multi-contaminant problems; design of process integration networks that targets heat and water recovery, interplant water integration and network retrofit analysis.

The insight-based techniques do not involve computational algorithms in generating solutions. However, they do require significant problem simplifications and assumptions (Wang & Smith, 1994a; Bagajewicz, 2000; El-Halwagi, et al., 2003; Manan, et al., 2004; Foo, 2009). Mathematical optimization on the other hand allows treatment of water network synthesis problems in their full complexity by considering representative cost-functions, multiple contaminants, and various topological constraints (Takama, et al., 1980; Salvetski & Bagajewicz, 2000b; Bagajewicz & Savelski, 2001; Grossmann & Lee, 2003; Gunaratman, et al., 2005). However, it suffers from high computational time required to achieve optimality, especially in large scale problems. The limitations of the graphical-based approaches brought about a huge interest in mathematical programming techniques. Mathematical optimization is considered easier to apply and also gives more elaborate objective functions in terms of cost and number of connection (Faria & Bagajewicz, 2010). However Shi and Liu (2011) argued that pinch-based methods explain problems graphically which makes it easier to understand. Feng & Seider (2001) also allude that mathematical programming is sometimes difficult to interpret leaving designers with limited insights as opposed to graphical methods. However, when dealing with multi-contaminant problems, graphical methods use assumptions for ease of implementation, some of which may be infeasible to justify, hence mathematical optimization has an added advantage, because it allows the treatment of large scale problems consisting of

multiple contaminants streams, which pinch-based techniques struggles to find feasible solution.

2.3.2 Mathematical-Based Optimization Efforts

Mathematical optimization is increasingly favored because of the disadvantages of graphical, heuristic, and algorithmic procedures to provide rigorous solutions to multiple contaminant problems (Takama, et al., 1980). Mathematical optimization allows the treatment of water network synthesis problem in their full complexity by considering representative cost functions, multiple contaminants, and various topological constraints (Takama, et al., 1980; Salvetski & Bagajewicz, 2000b; Bagajewicz & Savelski, 2001; Grossmann & Lee, 2003; Gunaratman, et al., 2005). A superstructure which is the superset of all feasible solutions is the basis of mathematical optimization techniques. A mathematical model is usually formulated based on the superstructure which usually results in an objective function which can be a linear programming (LP), mixed integer linear programming (MILP) nonlinear programming (NLP) or mixed inter nonlinear programming (MINLP) which is subject to minimization or maximization within the framework.

Takama et al. (1980) developed a seminal superstructure for water minimization through process integration. They proposed the integration of water using and treatment process into a single system where a mathematical model was developed for a fixed mass load. The model was solved and validated using a case study of a petrochemical industry allowing for all reuse and regeneration possibilities. The work of Takama et al. (1980) was later extended by Rossiter & Nath (1995) where mass transfer, based on fixed mass load and fixed outlet concentration was considered using nonlinear programming (NLP) to obtain an optimal solution. However, both Takama et al. (1980) and Rossiter & Nath (1995) considered small problems in their model validation, and could not give satisfactory results when applied to industrial problems of five or more streams. Their model also proved to require unacceptably long computational times to converge, which showed that the solution obtained converged at a local optimum.

In another effort Doyle & Smith (1997) proposed a new method to achieve optimal water reuse/recycle in process industry using a sequential procedure that adopts linear programming (LP) as an initial point to solve an NLP. Doyle & Smith (1997) considered two cases where the mass transfer is modelled as fixed mass load which was solved as an NLP problem, and fixed outlet concentration which was solved as a linear optimization problem (LP). This method sought to overcome previous water using operations where mass exchange characteristics of some contaminants to be modelled as fixed mass load or fixed outlet concentration leads to an overall nonlinear problem for which it is difficult to find a feasible solution. Additional constraints were added on maximum wastewater flowrates and forbidden stream matches to eliminate uneconomically small flowrates between operations and also aid solution convergence. However, the approach did not guarantee global optimum solution.

Feng & Seider (2001) developed a new water network superstructure with one or more internal water mains to reduce freshwater consumption and wastewater generation in a process industry. The work also shed light on the simplification of piping networks in large petrochemical or chemical industries. The water mains help in the simplification of operations and water quality control as well as design strategy. It reduces the amount of freshwater consumed and wastewater discharged into the environment. However, inclusion of multiple internal water mains leads to complexity of piping network especially in large industries which could lead to design problems.

Huang et al. (1999) proposed similar work to Takama et al. (1980) by developing a theoretical model for the design of water usage and treatment network for optimal use of water in a chemical plant. The proposed work was modelled as a mixed integer nonlinear programming (MINLP) with algorithms done to obtain a feasible meeting point or solution. Hence global optimality is not guaranteed. Karrupiah & Grossmann (2006) formulated a water minimization problem by proposing a superstructure similar to that of Takama et al. (1980) for the design of integrated water systems. Their proposed work incorporated water using and water treatment units in a single network. The network also included all possible

feasible design alternatives for water treatment, reuse and recycle. Although Karrupiah & Grossmann (2006) had initially formulated their problem as NLP, it was later reformulated as an MINLP. The problem was reported to be nonconvex due to bilinear terms in the constraints.

Ahmetovic & Grossmann (2010) proposed a strategy to improve the work of Karrupiah & Grossmann (2006) on the optimization of integrated process water networks. The proposed model was formulated as an NLP and MINLP using binary variables to determine piping interconnections, flowrates and contaminant concentrations of all streams in the water network to obtain global optimality. The binary variables also helped in determining the investment cost of piping in the network. The objective function of their proposed strategy was to minimize the total network cost which consisted of freshwater cost and capital and operating cost of treatment units. Although the work of Ahmetovic & Grossmann (2010) were aimed at improving the work done by Karrupiah & Grossmann (2006), the types and technology of treatment units were not specified, and a detailed synthesis of the treatment units was not reported. However, the investment cost and operating cost of treatment units was inclusive in the objective function.

Savelski & Bagajewicz (2000a) presented the necessary conditions of optimality for single contaminant water allocation planning problem (WAP) based on Wang & Smith (1994b). They stated that optimal structures satisfy monotonicity of the outlet concentration when one process sends its wastewater to other process units. Savelski & Bagajewicz (2000b) designed a water utilization network illustrating necessary conditions of optimality for single component in process plants. The work corresponds to the work on optimal water allocation planning problem with the objective to minimize the total freshwater intake, by considering wastewater reuse. In another effort Savelski & Bagajewicz (2001a) addresses the optimum design of water utilization systems based on a single contaminant. They used the necessary conditions for optimality based on an earlier work of Savelski & Bagajewicz (2000b) which allows for the formulation of LP and MILP. The proposed method when used for problems of different cases demonstrated multiple alternate solutions, including degenerate cases where flows through the

processes are much greater than the minimum required. The results showed retrofit for design possibilities of water utilization systems. A partial regeneration unit was incorporated into the system to further reduce freshwater usage.

Savelski & Bagajewicz (2001b) followed up their design work with an algorithmic method to design a water utilization network in refineries and process plants. This method was based on the earlier work of necessary and sufficient conditions of optimality (Savelski & Bagajewicz, 2000a). The method allows for the construction of a global optimal solution using a targeting procedure. The method was applicable to industrial cases where the concern is on a single contaminant such as pulp and paper industry where the contaminants of concern is suspended solids, the painting industry as well as the steel and semiconductor industries, where the major concern is on a single contaminant. These methods however, could not be used for cases of multiple contaminants and was not robust.

In an extension to their work in 2000a, Savelski & Bagajewicz (2003) presents the necessary conditions for optimality for multicomponent water allocation systems in refineries and process plants. They argued the multicomponent problems display multiple suboptimal solutions, hence global optimality cannot be guaranteed by solving these problems directly. Hence, they proposed an algorithmic procedure that are capable of solving the problem in a robust manner and also guarantees global optimality. In another development Faria & Bagajewicz (2008) propose a method to address the problems of nonlinearities and non-convexities due to bilinear terms. In their formulation, they discretize one of the variables of the bilinear terms generating an MILP model which was solved to produce a lower bound as a starting point for the NLP model. They also adopted an internal elimination method in order to reduce the gap between the lower bound and the upper bound. This resulted in the shrinking of the feasible region until a global optimum was reached. A regeneration unit was embedded in their proposed model to enhance wastewater quality for reuse. However, the type of regeneration technology was not clarified and detailed model of the regeneration unit was not conducted and included in the overall cost of the objective function.

Gabriel & El-Halwagi (2005) used the source-interceptor-sink framework to develop a water network superstructure to minimize cost of freshwater and wastewater as well as interception unit cost. Their original formulation resulted in an MINLP, hence could not guarantee global optimality. Gabriel and El-Halwagi (2005) employed a number of simplifying assumptions to reformulate the model into a linear programming. They used the concept of decomposition of source streams into substreams. They argued that, the aim of stream separation assists in avoiding the loss of separation driving force as a result of mixing and also to prevent cross-contamination of streams as a result of introducing pollutants from one stream to another. This helped in eliminating the nonconvex terms in the mass balances. They also discretized the interception devices into a number of interceptors to match the performance of the original interceptor. Gabriel and El-Halwagi (2005) were able to determine the cost of interception devices separately from the optimization formulation and transformed it into a pre-synthesis task. The general model was therefore reformulated into an LP which was solved globally. Their formulation was limited to single contaminant problems and also the assumption of not allowing mixing of streams in an interception unit could lead to more than the minimum number of interceptor units.

Nápoles-Rivera et al. (2011) extended the work of Gabriel and El-Halwagi (2005) to solve for a case with multi-contaminant and to minimize the number of interceptor units. Their formulation considered direct recycle and includes in-plant interceptors for terminal treatment systems. Their proposed model resulted in a nonlinear and nonconvex problem. Hence, a two-tier approach was adopted to simplify the superstructure. Nápoles-Rivera et al. (2011) solved a pre-synthesis problem to identify the performance and cost of the interceptors with specific tasks and representation that avoids the mixing of different streams in a treatment system. This lead to a linear relationship of the mass balances, and the model was solved to global optimality. Their proposed model was applied to an industrial case study of a refinery system and the results indicate significant reduction in fresh resource consumption and waste generation as compared to a model without regeneration. Although, Nápoles-Rivera et al. (2011) proposed work showed a significant reduction in freshwater usage, and number of cost treatment units, the

overall costs of the wastewater network superstructure did not reflect in their representation of the water network. Detailed synthesis of the treatment units were not conducted to include in the objective function. Also there is a likelihood of contaminant accumulation in process units as direct recycle/reuse was practiced in the system.

Poplewski et al. (2010) addresses the problem of a water using network that consists of fixed flowrate water using processes. Poplewski et al. (2010) formulated a mathematical model based on a superstructure which resulted in an MILP. The proposed method allows for the use of model to solve for a case of multi-contaminants accounting for various technical and economic data. The model also shows alternative solutions for minimum freshwater intake and cost of piping interconnections. The results gave insights to a data for the design of a simple water network with reduced number of connections with an additional freshwater intake. The increase in freshwater intake resulted from the fact that, the proposed method did not include regeneration hence the only avenue for freshwater reduction was through direct reuse/recycle. Environmental effluent discharge limits was not considered in the overall water network design.

In another development Poplewski et al. (2011) addressed water usage network problem with regeneration processes based on an earlier work of Jezowski et al. (2007). Poplewski et al. (2011) considered multiple contaminants and two types of water using process units in their model formulation. A simultaneous approach was used with a single algorithm to solve an MINLP problem using metaheuristic optimization-adaptive random search method. Their method catered for minimization of piping interconnections and elimination of regeneration recycles. The solution procedure for dealing with equality constraints within the formulation of an optimization problem is general for any metaheuristic method Poplewski et al. (2011). The regeneration units in the method were solely to enhance wastewater quality for reuse/recycle. Environmental limits for effluent concentrations were not taken into consideration, hence the method is deemed unsustainable. Also detailed mathematical modelling of the regeneration units was not conducted and included in the overall objective function so the cost of the

water network cannot be said to be a true representation of the overall water network.

Teles et al. (2008) developed a superstructure for the optimal design of a water network that accounts for all possible design connections between water sources and sinks. Different structures were generated that consider all possible operational sequence during optimization. Teles et al. (2008) did not however consider treatment units neither in an integrated way nor as part of a downstream system required to lower the concentration of streams to the discharge limits. Their model was solved with a succession of linear programming techniques. The overall water network superstructure was designed with the water using units arranged in parallel. Although the developed model was aimed at optimal use of freshwater intake, considerations for water reuse/recycle and regeneration which is the basis for freshwater saving and wastewater minimization was not included in their proposed model. Environmental effluent discharge limits/considerations were not taken into account hence the proposed work could not said to be cost effective and sustainable.

Teles et al. (2009) presented a two tier algorithm method for the optimal design of water-using network with multiple contaminants using fixed contaminant load and fixed flowrate methods. Teles et al. (2009) used a two-phased procedure for their solution algorithms where an initialization is taken place before the optimization of the standard nonlinear programming problem. The formulation was based on the superstructure that includes all possible design alternatives for freshwater use and wastewater reuse and recycling. Teles et al. (2009) used sequential solution of mixed integer linear programs to generate starting points, where binary variables were used in selecting the most appropriate units in terms of minimum freshwater consumption. The sequential solution procedure circumvents the need for bilinear terms by ensuring that the concentration of all possible inlet streams to one calculation stage are known based on results of previous stages. Teles et al. (2009) discovered that both fixed load and fixed flowrate have a single starting point, they gave a solution based on local optima hence multiple starting points are desirable to avoid local optima. Teles et al. (2008) reported that their

algorithm is very effective in escaping local optima, which requires significantly less computational time and can be applied to large scale problems. They added that their method proved to be faster in order of magnitude compared to the global solver BARON.

Tudor & Lavric, (2010a) proposed a design of an integrated water network combining water using units and treatment units - and optimized it using Genetic Algorithms by targeting for maximum treated water reuse in order to minimize freshwater consumption. Their model was tested against a case study with six water using and three treatment units dealing with three contaminants. The results were compared against a water network with only water-using units' in terms of freshwater consumption, network length, and operating cost. It was observed that the integrated water network (IWN) reduced 55% of freshwater demand compared with the water using network. An IWN also uses less number of pipes than the water-using network. This has a major impact on investment costs and, also, on operating costs, since lesser pipes means lesser energy consumed for pumping. However it was observed that in terms of overall costs, the water-using network was much cheaper than the integrated water network. This was as a result of including the costs of wastewater treatment units for reuse and also the cost of pumping of streams to other process units, whereas the water-using networks did not have treatment units and only accounted for costs of pumping and effluent treatment for environmental discharge limits. However, their work did not consider regeneration for reuse/recycle and also detailed cost analysis of the treatment units was not conducted and included in the overall objective function.

In another development, Tudor & Lavric (2010b) developed an optimization model for the integrated water using (WU) and water treatment units (TU). The work considered maximum treated water reuse as an alternative to freshwater usage. The model developed was based on total and contaminant species balances focusing on three main things. Firstly, the WN without a treatment unit is optimized using supply water as an objective function. The second part dealt with optimization of integrated water network (IWN) which was compared with the previous case and the third part looked at contaminant data analysis.

Contaminants' mean availability and networks reuse index was conducted. The developed model was solved using genetic algorithms (GA) such that significant amount of freshwater consumption was reduced, and as a result the total IWN cost was reduced. However, detailed model of the treatment units were not included in the overall water network objective function and type of treatment units were not identified. Hence the cost reported in the paper could not have been justified to be a true representation of the total water network.

Tudor and Lavric (2011) in another development used genetic algorithm for the dual-objective optimization of an integrated water/wastewater network by targeting for freshwater minimization while reducing operating costs at the same time. The formulation resulted into a nonlinear mathematical model which comprises of total and partial mass balances together with piping diameter and interconnections observing optimal investment and operating costs. Tudor and Lavric (2011) arranged the water-using and treatment units in a certain criterion in order to achieve a constant driving force throughout the integrated water/wastewater network. The dual-objectives are contradictory, thus leading to a set of alternative solutions which are equally optimal known as the *pareto front*. This is in contrast to the conventional freshwater consumption reduction with concerns of identifying the opportunities for wastewater reuse, at the expense of increasing the complexity of the pipe and network superstructure. Tudor and Lavric (2011) however, did not include possibilities for internal recycles or through the treatment units. Hence all freshwater reduction opportunities were not explored. Also detailed cost analysis of treatment units were not conducted to include in the overall cost of water network superstructure.

2.4 Membrane Systems

Membranes are thin layer materials that have the capability of separating materials based on their physical and chemical properties (Srathmann, et al., 1997). The separation of materials in membranes is carried out as a result of a driving force applied across the membrane system. Membranes in appearance can be solid or liquid. Membrane separation systems operate by separating a feed stream into a cleaner stream called the permeate stream, and a highly concentrated stream that

takes contaminants from the permeate stream called retentate or concentrate stream. Membranes can be used to separate components of different range of particle sizes and molecular weights, from macromolecular materials such as starch and protein to monovalent ions. The separation mechanisms of membrane systems are dependent on size exclusion, pore flow, and solution diffusion (Anon., 2015). The mechanism of size exclusion is based on the principle that membranes material must have pores or holes of a certain size such that certain species can pass through and others cannot. The mechanism of pore flow is based on the principle of selective retardation where the pore diameter of the membrane material is close to molecular sizes. And thirdly the mechanism of solution diffusion is based on the principle where migration into the membrane by molecular diffusion and the re-emergence from the other side.

The main properties that determine membrane performance are high selectivity and fluxes, good mechanical, chemical, and thermal stability under operating conditions, low fouling tendencies and good compatibility with the operating environment as well cost effective and defect free operation. The key applications of membranes apart from production of portable water and separation of industrial gases are that, they can be used for other important applications such as filtration of particulate matter from liquid suspensions, air or industrial flue gas and dehydration of ethanol azeotropes. Membranes are used in specialized application such as separation of electrochemical processes, dialysis of blood and urine, artificial lungs, controlled release of therapeutic drugs, membrane-based sensors etc.

2.4.1 Types of Membrane System

Membranes can be identified and grouped based on their nature, structure or driving force. Based on the driving force membrane separation processes can be classified as Pressure driven, electrical driven, concentration gradient, temperature driven, and processes with combine driving forces as illustrated in Figure 2.16.

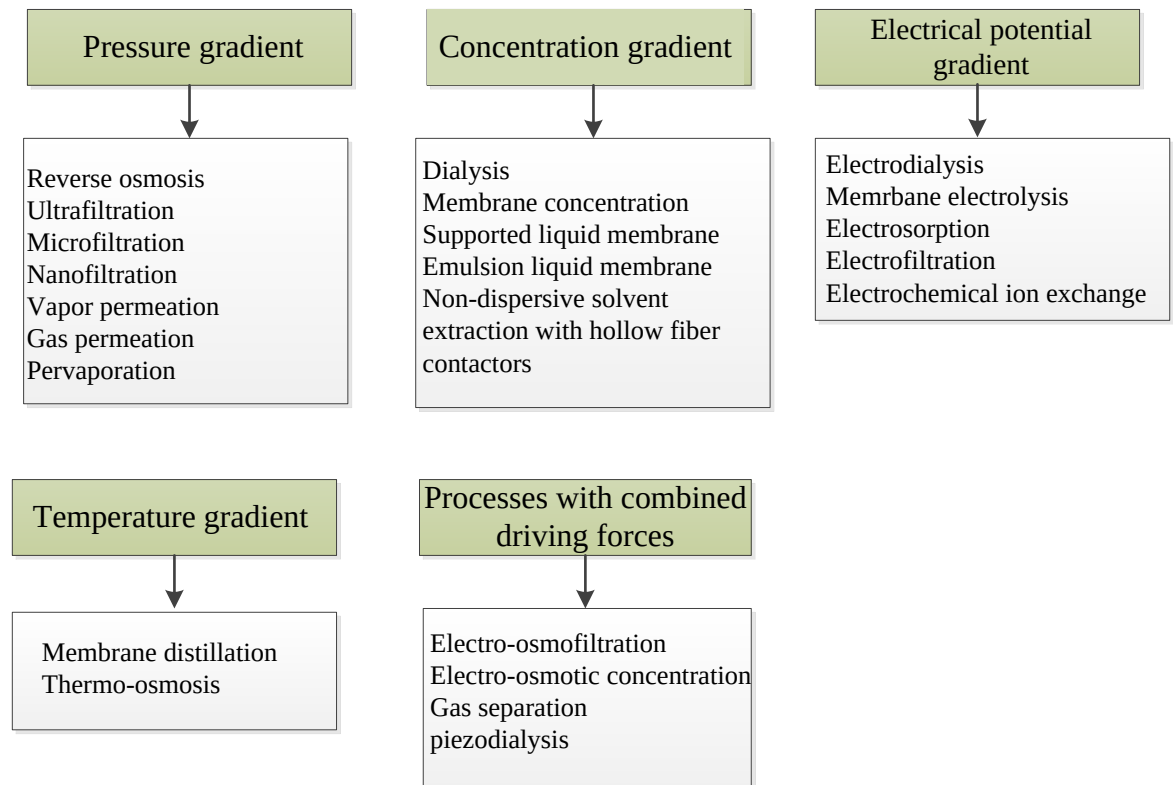


Figure 2.16: Classification of membrane separation processes

Pressure gradient. These are membrane systems which use the difference in pressure as a driving force for mass transfer across the membrane system.

Concentration gradient. The mode of transport in the concentration gradient membrane systems is instigated by the difference in concentration of solution in a membrane system.

Electrical potential gradient. They use electrical potential as the driving force for contaminants removal across the membrane system.

Temperature gradient. Separation is induced by a vapor pressure gradient that arises from a temperature difference across the membrane.

Sometimes, a combination of the processes gives rise to a new membrane called *combined driving forces membrane systems*. Electro-osmofiltration, which is a combination of a pressure driven, and electrical driven membrane processes,

electro-osmotic concentration is a combination of electrical driven and concentration driven processes. Others are Gas separation and piezodialysis which are a combination of pressure driven and concentration driven processes.

Membrane technology has increasingly become one of the main water treatment technologies in the quest to solve water shortage problems through sea/brackish water desalination, wastewater treatment and regeneration reuse/recycle. The application of membrane technologies for water and wastewater treatment has been hindered by fouling of membrane material due to the presence of suspended solids, colloidal material, organics, bacteria or scale from dissolved ions (Strathmann, et al., 1997). The use of membrane technology for water treatment as well as regenerators for wastewater treatment in process industries has increased over the years. This is due to the increased regulatory pressure to meet potable water standards, increased demand on existing but overly exploited water bodies. Market forces governing the development and commercialization of the membrane technologies also contribute to the global increase in the use of membrane technologies for water and wastewater treatment (Mallevalle, et al., 1996). However, Durham, et al. (2001) maintains that the most realistic issue when it comes to membrane technology for reuse/recycle, wastewater treatment and desalination of brackish water is the integrity of the membrane application systems. Membrane integrity is the ability of the membrane system to operate effectively without allowing reject stream to leak into product stream through breakages or inadequate scaling. This work proposes to use the industrially favored reverse RO and ED as membrane partitioning regenerators in a water network.

2.4.2 Electrodialysis Membrane Systems

Electrodialysis is considered to be the first membrane based water treatment technology which became commercially available over the past four decades. Industrial applications of ED include brackish water desalination, boiler feed and process water treatment, wastewater treatment, demineralization of food products, and table salt production (Strathmann, 2010). ED, in principle, is based on the electromigration of ions through cation and anion exchange permselective

membranes, which allow the passage of positive and negative ions respectively (Korngold, 1982; Tsiakis & Papageorgiou, 2005). ED processes for water desalination are in direct competition with distillation, reverse osmosis, and recently nanofiltration in the industry (Strathmann, 2010). However it has a competitive edge over the above mentioned desalination processes in a certain range of feed water salt concentration (Strathmann, 2010). ED uses direct electric current for the transfer of ions in the solution hence energy consumption and the required membrane area increases with increasing feed water concentration (Korngold, 1982). The high cost for saline water desalination, calls for optimal configuration of an electrodialysis unit. This can be done by determination of number of fixed parameters and a number of variables that affect the operation and the economics of the process. Minimising the cost of desalination of an ED unit translates to the reduction of energy requirements for achieving the targeted result.

Operation Principles of ED Unit

Figure 2.17 shows a schematic diagram of an ED system. It consists of anion and cation exchange membranes arranged in series in an alternating pattern. The alternating membrane arrangement is sandwiched between an anode and cathode to form individual cells. An ED cell operates when feed water is pumped through the cells accompanied by electrical potential.

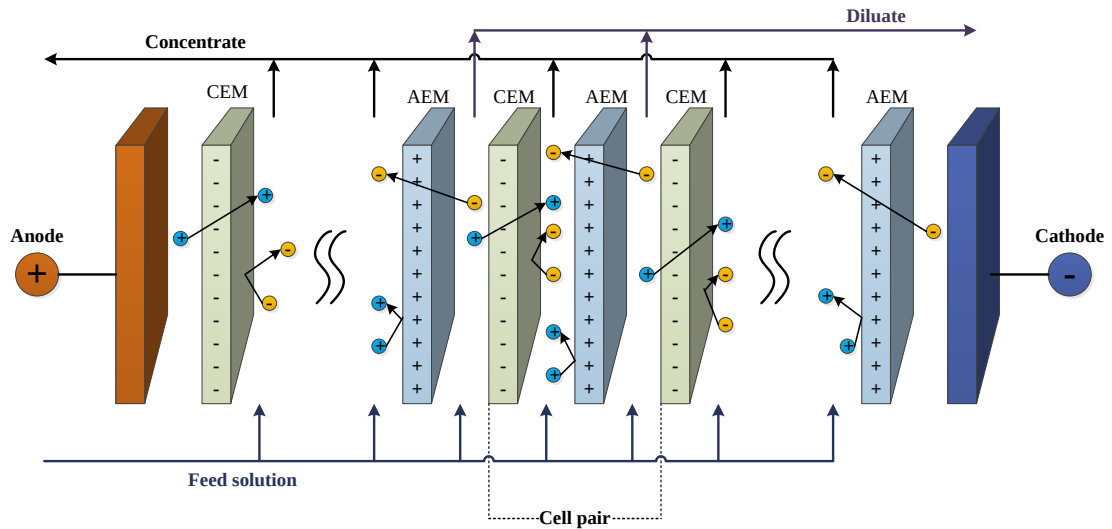


Figure 2.17: Schematic of an electrodialysis system

Once an electrical potential is established between the electrodes, positively charged ions move towards the cathode and the negatively charged ions move towards the anode (Tsiakis & Papageorgiou, 2005). The cation exchange membrane allows cations to pass through easily which are retained in an anion exchange membrane channel. Likewise, anions pass through anion exchange membrane and are retained by the cation exchange membrane (Farrell, et al., 2003). This results in an increase in ion concentration in both membrane compartments, resulting in a decrease in ion concentration in alternate compartments. The solution that loses its ions is called a diluate solution and the compartment is referred to as demineralising stream whereas the solution that gains the ions is referred to as concentrate stream (Schaffer & Mintz, 1980; Strathmann, 2010; Valero, et al., 2011). The feed water through an ED system is separated into product water which has a tolerably low conductivity and total dissolved solids level, the concentrate stream, which is the water concentrated with ions from the feed water ions, and electrode feed water which is the water that passes directly over the electrodes that creates the electrical potential (Valero, et al., 2011).

Spacers are inserted between the diluate and concentrate compartments which represent a flow path for both streams. They contain manifolds to distribute process fluids in the compartments. Spacers are also used to provide sufficient mixing of solutions at the membrane surfaces and should cause negligible pressure loss (Valero, et al., 2011; Tsiakis & Papageorgiou, 2005).

The applied electrical potential is the driving force for the ion transfers in an ED process. The concentrate and the diluate compartment and the anion and cation exchange membranes make a cell pair, which are the basic building blocks of an electrodialysis membrane stack (Valero, et al., 2011). Each membrane stack is made up of two electrodes and group of cell pairs and the amount of ions to be removed by an electrodialysis system is directly proportional to the configuration of the membrane stack (Strathmann, 2010). The top and bottom of a membrane stack are clamped with metal steel plates that compress the membranes and spacers in order to prevent leakage inside the stack.

An ED unit maybe operated in batch type, continuous, or in a feed and bleed mode with minimal recycle of both diluate and concentrate stream, depending on the feed solution concentration and product water requirement. Regardless of the mode of operation, an electrodialysis unit can be operated in two basic concepts; unidirectional or electrodialysis reversal (Strathmann, 2010). A unidirectional electrodialysis unit consist of a permanent electric field in one direction with a fixed a diluate and concentrate cells operating permanently (Srathmann, et al., 1997). Electrodialysis units operated in unidirectional processes are susceptible to membrane fouling and scaling and usually require pretreatment of feed water and periodic cleansing of stacks with acid or detergent solutions (Valero, et al., 2011). This concept of electrodialysis process is out dated and has longed been phased out (Valero, et al., 2011).

In ED reversal operating mode, the polarity of the electric field applied as the driving force for the transfer of ions is reversed in some time intervals which reverse the flow streams allowing the diluate cell to become the concentrate cell. This causes the fouling on the membrane surface to dissolve and be removed by the flow stream passing through the cell.

Design of an Electrodialysis Unit

The design and operation of an ED unit are based on a set of fixed and variable parameters such as stack construction, feed and product water quality, membrane properties, flow velocities, current density, area, current density to name but a few (Lee, et al., 2002). Korngold, (1982) conducted an investigation to determine the energy requirement of an ED unit for certain concentration range. Korngold (1982) stated that in order to optimise an ED unit certain considerations have to be made as follows:

- (i) The diluate cell must be thin.
- (ii) Pressure between diluate and concentrate must be kept at low as possible so as to prevent mechanical stress on the membrane material.
- (iii) Proper scaling properties of the cell and membrane material should done in order to prevent leakage.
- (iv) The cell material must have good mechanical properties and good structural stability.
- (v) The flowrates across each unit should be evenly distributed and pressure drop across the unit must be at minimal.

Korngold, (1982) went further to state that the energy requirement of an ED unit is depended among several parameters, current density, membrane resistance, cell thickness, type of spacer, concentration of feed, and temperature.

Hattenbach & Kniefel, (1986) developed a mathematical model of an ED unit to determine the effect of cell thickness and flow velocity on the product water cost. They used a computer programme to calculate the results and reported that the reduction of cell thickness to 0.2mm with a corresponding flow velocity of 0.13-0.17m/s yields a minimum cost of product water. Such scaling of membrane cell thickness is however not practical, since it will require sophisticated techniques to develop membrane materials with cell thicknesses within the range of 0.2mm, hence they recommended 0.4 – 0.6mm cell thickness for industrial development.

Kraaijeveld, et al., (1995) developed a mathematical model for a batch-mode ED unit based on the diffusion of ions across the membranes. They used the Maxwell-

Stefen equations to describe the mass transfer resistances of the membranes and the diffusion films on either side of the membranes. They considered diffusion transport mechanism in their model development and did not consider other transport mechanisms. Nikoneko, et al., (1999) developed a model to determine the cost of an ED unit using the convective-diffusion model. They used a mathematical simulation, based on regression of experimental data for cost estimation of the process at optimum operating parameters. They assumed both diluate and concentrate channels do have spacers but high smooth surfaces.

Lee et al. (2002) presented a detailed mathematical model of an ED unit, taking into consideration the limiting current density based on experimental results. They based their development of the model on some assumptions on the flow characteristics, which resulted in the avoidance of experimental determination of diffusion coefficients. The developed model was applied to a case study involving brackish water with a single contaminant and the optimum results was presented. Although they provided a flowsheet illustrating the calculation procedure for an ED unit, the work did not show the platform in which the developed model was applied to the case study. Tsiakis & Papageorgiou (2005) extended the work of Lee et al. (2002) for a multi-stage ED unit. They adopted a feed and method for a continuous operation of the ED unit. The model was applied to a case study involving a single contaminant and was solved in GAMS/BARON to obtain optimal design variable and total annualised cost in terms of capital and operating cost.

2.4.3 Reverse Osmosis Membrane Systems

Reverse osmosis is a pressure-driven membrane separation process. Pressure-driven membrane systems selectively allow the passage of one or more species through the membrane unit. Figure 2.18 shows a schematic diagram of a reverse osmosis system.

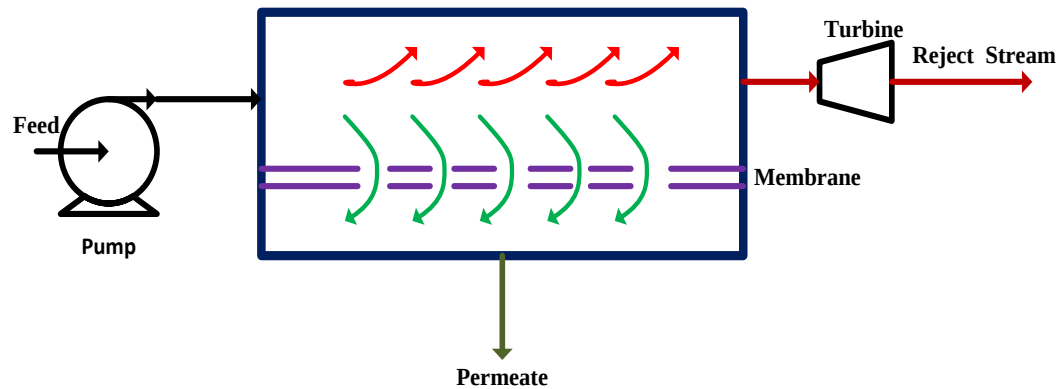


Figure 2.18: Schematic diagram of a reverse osmosis unit

In a RO system the stream retained at the high pressure side is called the retentate, while that driven to the low pressure side is called the permeate stream (El-Halwagi, et al., 2003). RO is based on the principle that takes place when an external pressure greater than the osmotic pressure is applied to a solution causing a preferential passage of solvent, leaving pollutants in the reject stream (El-Halwagi, et al., 2003).

Industrial applications of RO include desalination of salts, organics, ions, and heavy metals. However recent applications involve its use for municipal and industrial wastewater treatment, and as partitioning regenerators to enhance water recovery through reuse/recycle in the process industry (Garud, et al., 2011). Reverse osmosis has gained growing industrial favour over the past years in order to meet several objectives such as water purification, saline water demineralization, boiler feed water treatment, as well as environmental applications (El-Halwagi, 1992; Saif, et al., 2008). Most industrial applications of reverse osmosis systems are preceded by pre-treatment units to remove suspended solids and colloidal matter. Chemicals are also added to control biological growth and reduce scaling. However, recent advancement in membrane technology has seen robust membrane materials that are resistant to biological growth, scaling, and fouling. RO processes also have an added advantage where turbines extract energy from the high pressure reject streams. There are three main configurations within the RO domain: hollow fibre, tubular, and spiral wound (Garud, et al.,

2011). Hollow fibre RO units have received considerable industrial favour over the rest. This is due to the added advantage of large-surface-volume ratio, self-supporting strength of fibre, negligible concentration polarisation near membrane surface, modular and compact, and relatively cost effective (El-Halwagi, et al., 2003).

Operation Principles of Hollow Fibre Membrane System

A hollow fibre reverse osmosis (HFRO) unit is housed by a shell. The fibres are grouped in such a way that one end is opened to the atmosphere and the other end sealed. The open end of the fibres are potted into an epoxy sealing head plate after which the permeate stream is collected (El-Halwagi, et al., 2003). When the feed solution is pressurised into the hollow fibre reverse osmosis unit, the solution flows radially from central porous tubular distributor. As the feed solution flows towards the shell perimeter, the permeate solution penetrates through the fibre wall by the process of reverse osmosis into the bore side. The permeate solution is collected at the shell side of the fibres whereas the reject solution is collected at the porous wall of the shell.

Design of Hollow Fibre Membrane Systems

A detailed understanding of the operating principles and modelling of HFRO unit is important to guide the optimal design of the system. Two approaches have been adopted to determine the pressure variations on the shell side of the HFRO unit (El-Halwagi, et al., 2003). The first approach relates to the design of the HFRO unit where the shell side pressure is assumed to be a constant. Ohya, et al. (1977) conducted an experimental analysis of the HFRO unit to obtain some characteristics of the unit. They showed that the water permeability constant is largely dependent on pressure which has a tendency of affecting the solute flux constant as pressure increases. They also maintained the pressure on the shell side as constant. Gupta, (1987) developed an analytical equation for a radial-flow fibre reverse osmosis unit assuming a constant shell side pressure. They used the developed equation in their work to analyse the experimental data of Ohya et al. (1977). They showed that the results obtained by the design are accurate and

easier to work with compared to the one reported by Ohya et al. (1977). They concluded that the design equations can be used as a starting point for the design of HFRO system.

The second approach uses Darcy's equation with an arbitrary empirical constant where the fibre bundle is treated as a porous medium (El-Halwagi, 2003). Dandavati et al. (1975) conducted detailed experimental work to analyse radial flow of HFRO units. Their work targeted the analysis of solvent and solute permeability coefficients of a hollow fibre bundle. They concluded that determining the solute and solvent permeability in a HFRO guides towards the productivity and product concentration respectively. Hermans (1977), developed a mathematical model for an HFRO unit to analyse the physical aspects pertaining to the design of a hollow fibre model. The author pointed out that the quantitative and semi-quantitative description of the process should be conducted in order to understand the effect of fibre length, fibre diameter, packing density, and flowrates to name but a few on the operating principles. El-Halwagi (2003) developed a mathematical model of HFRO unit using the membrane transport equations and the hydrodynamic modelling of the RO module. The membrane transport equations relates to water permeation and solute flux taking place at the membrane surface whereas hydrodynamic modelling relates to the macroscopic transport of various species along with momentum and energy associated with them (El-Halwagi, 2003). The author adopted the water flux and solute flux equations from the work of Dandavati et al, (1975) and Evangelista, (1986). Equations for permeate flowrate and concentration were also illustrated in the formulation.

2.5 Integrated Water and Membrane Networks

Recent efforts in the area of process integration for wastewater minimization in the process industry have been focusing on the use of mathematical optimization models. These approaches usually involve a water network synthesis based

superstructure representation of design alternatives using membrane regenerators (Ng, et al., 2007; Tan, et al., 2009; Khor, et al., 2011; 2012)

2.5.1 “Black-box” Regeneration Models

A “black-box” water regeneration model is water network regeneration in which the regeneration unit is characterised by the performance (Removal ratio) and linear cost function. The type of technology of the regeneration unit is sometimes mentioned in text however its performance cannot be differentiated from other treatment technologies. Galan & Grossmann (1998) states that some conventional treatment technologies such as biological, chemical and physical can be represented by their performance equations, membrane technologies will however not be suited for such approximations. Chew et al. (2008) integrated a single regenerator for the treatment of multi-contaminants in an interplant water integration system using direct and indirect integration. In their presentation, the cost of regeneration is represented by the capital cost of the unit, linear function of throughput, operating cost and linear function of load removal.

Feng et al, (2007) developed a mathematical model using grass-root design approach for regeneration recycling within a water network superstructure. They used sequential optimization approach to solve a multi-objective problem with the aim of minimising freshwater consumption, regenerated water flowrate and contaminant regeneration load. Feng et al, (2007) considered that regeneration units will vary in capital and operation cost hence it is necessary to include weighting coefficient to describe the cost and performance of the different regeneration units. Weighting coefficient was introduced to express the inequivalence of different contaminants within a stream. Although Feng et al, (2007) formulation was novel and added insight into the field of process water management, their formulation did not include complex and variable economic factors and only considered basic parameters of a water system. They did not also specify the type of regeneration units employed for their work and the formulation considered the “black-box” approach which does not give true cost representation of the regeneration units.

Tan et al. (2009) presented a novel superstructure approach similar to that of Ng et al. (2009) for the synthesis of water network for a single contaminant with a single partitioning regenerator which allows for possible reuse/recycle of both permeate and reject stream from the regenerator. Unlike Ng et al. (2009) who concentrated their efforts with identifying optimal water target or demand before the design of a detail water network, Tan et al. (2009) developed a superstructure which synthesizes and allows for contaminated streams from processes to be pooled before being sent to the regenerator for treatment. The superstructure representation allows determination of the optimal solution while generating network configuration simultaneously for optimal level of resource conservation. In their study they stated that about 35-59% of the reject stream from the regenerator is reused in other processes, which shows that total freshwater usage is much less if the water from the reject stream is not discarded as waste. Although, Tan et al. (2009) reported on the use of about 35 - 59% of reject stream for other process, there was no proper representation on the amount of freshwater cost that has been saved. Their model did not also account for the detailed cost of a superstructure including piping and its interconnections.

Tan et al. (2009) did not consider a detailed cost analysis of the membrane regeneration system taking into account operating and capital costs of the membrane system. Embedding the total annual cost of the water network superstructure in terms of freshwater and effluent treatment costs, based on their flowrates and piping interconnections gives a true representation of the total investment cost of the water network superstructure which can be minimized to give the optimal operation cost.

In an extension to their work in 2011, Khor et al. (2012) developed a water network superstructure to address the problem of water network regeneration synthesis. They incorporated multiple membrane and non-membrane regenerators. The proposed model includes determining splits fractions of source flowrates, regeneration potential, mixing ratios of sources and regenerated streams, which are subject to compliance with maximum allowable inlet contaminant concentration limits of sinks and discharge regulations. Khor et al., (2012)

extended the superstructure development by incorporating other treatment sinks to cater for untreated waste by incineration, which does not meet environmental discharge limits, and also waste sinks for deep ocean discharge of brine from the reject stream. Linear models were developed for membrane regeneration with fixed removal ratios and the addition of linear logical constraints using binary variables in order to tighten and enhance the formulation of solution convergence.

The source-regenerator-sink superstructure allows for all possible interconnections catering for water reuse/recycle, regeneration-reuse, and regeneration recycle. The model allows for water to be passed through the same regenerator or different regenerator for multi treatment in order to meet sink requirements for reuse /recycle or environmental discharge limits. This gives rise to a complete water network, where end-of-pipe effluent system is attached to the sinks before being discharged to the environment. Their overall water network superstructure optimization obtained a global optimal water network topology with a saving of 27% in freshwater use. They, however, did not include a detailed synthesis of membrane regenerators to obtain total annual costs (TAC) which comprise of the operating and capital costs of the membrane regenerators. Total synthesis of membrane regenerators will give a true representation in terms of number of membrane modules and operation of life of membranes.

In between the “black-box” formulation and detailed model (white-box) is a representation called the ‘Grey-box’. The ‘Grey-box’ simply describes a regeneration model which uses certain equations of the regeneration unit to describe it. The equations are assumed to be important equations that relate the performance of the regeneration units. Galan & Grossmann (1998) considered non-dispersive solvent extraction as the regeneration technology using short-cut models to describe the unit performance. Faria and Bagajewicz (2010) presented a nonlinear short-cut models for the cost of regeneration in a water network. Although, the cost representation of the regeneration unit is not linear, the formulation did not incorporate detailed model of the regeneration units. In a more recent development, Yang et al. (2014) showed a unifying approach by combining multiple water treatment technologies capable of treating all major contaminants.

The work focused on unit specific short cut cost functions in order to gain detailed understanding of trade-offs between removal efficiency of treatment units and the cost of the units, as well as the impact on the unit design.

2.5.2 Detailed Regeneration Models

The “black-box” and short cut (Grey-box) models do not give accurate representation of the regeneration units, hence there is a need to consider detail formulation of the regeneration units to incorporate in the water network superstructure. This approach will therefore give accurate representation of the energy consumption and associated cost of the regeneration units as well as optimal design parameters. Khor et al. (2011) addressed the gap on the work of Tan et al. (2009) by developing a detailed model representation for water network regeneration synthesis using MINLP optimization framework to obtain a rigorous cost-based relation between membrane regenerator and the overall superstructure. In their effort, Khor et al. (2011) incorporated the concepts of regeneration reuse/recycle and considered fixed flowrate water using processes, as opposed to the more traditional mass transfer-based fixed contaminant load models. The overall optimization of the proposed work leads to cost of water regeneration network that is a true representation of minimum cost as compared to other efforts that used a simplified “black/box”. Khor et al. (2011) argued that the proposed model could be applicable to multiple regenerators. However they did not incorporate multiple membrane regenerator units in their work. The proposed formulation should have included multiple regenerators in series or parallel so as to minimize the burden of passing all contaminants streams that need treatment to the single regenerator. Buabeng-Baidoo & Majozzi (2015) presented a detailed model of a reverse osmosis network (RON) within a water network superstructure. They synthesize the RON together with the overall water network for simultaneous water and energy minimization together with operation and capital cost. In another development, Mafukidze & Majozzi (2015) address the synthesis and optimization of an integrated water and membrane network. The work focuses on embedding a detailed model of the ED unit in the overall superstructure for water and energy minimization. The overall superstructure is

optimized to get the optimal water network superstructure and optimal design parameters of the ED subnetwork.

2.6 Challenges of Water Network Synthesis and Optimization

Computation and modelling of water network synthesis is faced with among other challenges non-convexity which is due to bilinear terms owing to the large number of economical, topological, component and mass balance constraints leading to multiple suboptimal solutions and non-optimal stationary points.

2.6.1 Convexification

Nonlinear, nonconvex problems arise due to the presences of bilinear terms and integer variables in the problem. The effect of this is the existence of multiple local minima that could potentially trap the optimisation routine. Linear programming (LP) optimisation problems are much easier to solve than NLP and MILP models. This is as a result of the nonlinearities in the NLP models and the presence of the 0-1 variables in the MILP models. LP models have a convex objective function and linear constraints which form a convex set hence a linear problem is generally guaranteed to converge to a globally optimal solution within a finite number of iterations (Edgar & Himmelblau, 1988). A convex nonlinear model will still guarantee global optimum, although will require more iterations to attain global optimality. Problems arise when the nonlinear function is non-convex. The presence of nonlinear, non-convex, bilinear terms is one of the major challenges in water network synthesis, especially in load balances as a result of contaminant mixing in water regeneration units (Khor, et al., 2014). Non-convexity within an optimisation model can lead to two of many problems such as; formulations of NLP sub problems resulting into multiple local optima as shown in Figure 2.19. Also MILP master problem may cut-off from global optimum as can be seen in Figure 2.19.

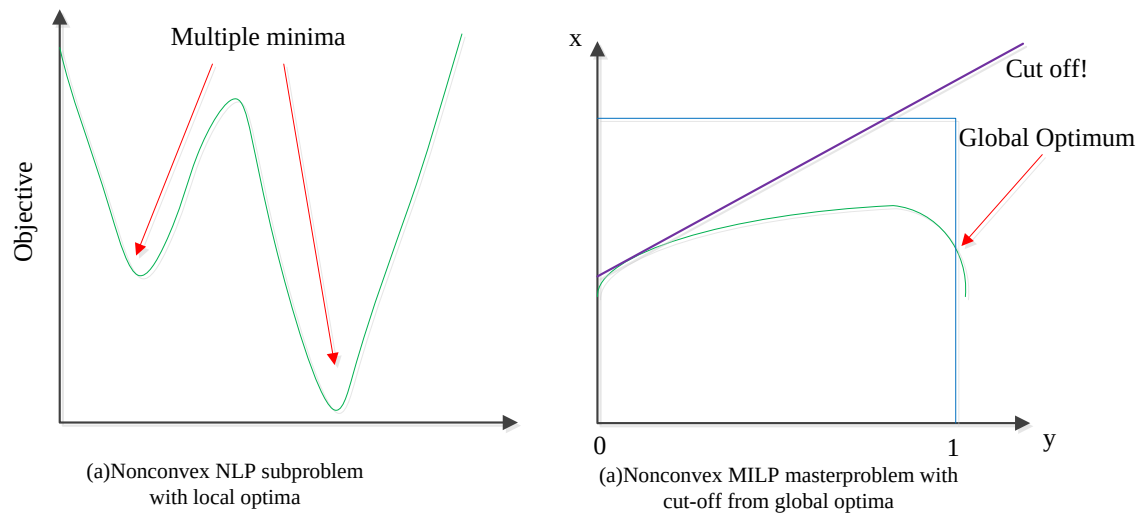


Figure 2.19: Non-convex NLP and MILP sub and master problems (Grossmann, 2014)

Convex estimators are usually employed to solve nonconvex problems. This is done by 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). The convex estimator forms the basis for most of the available relaxation techniques for nonconvex NLP and MINLP problems. The convex estimator linearization technique can be achieved by either directly replacing each nonconvex function with a convex under estimating function or by using transformations to generate new variables and convex constraints that exactly approximate the nonconvex function. Figure 2.20 illustrates a convex envelope for a nonconvex function.

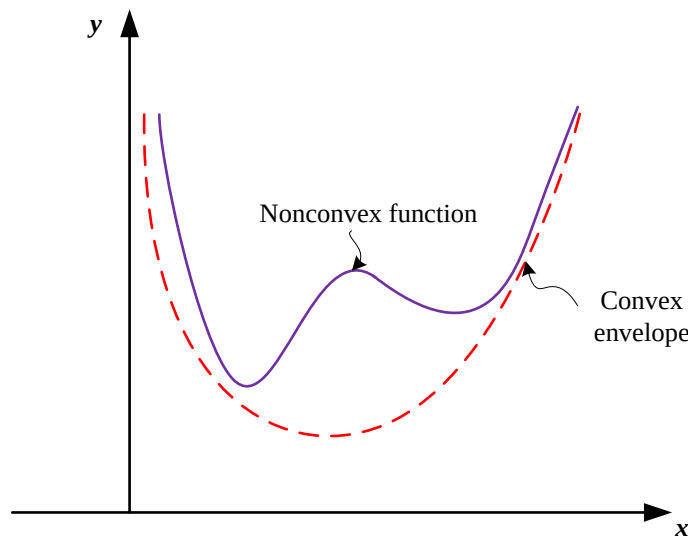


Figure 2.20: A convex envelope for a nonconvex function

2.6.2 Optimization Algorithms

The most common nonlinear non-convex problems in mathematical optimisation framework are MINLP problems. MINLP problems have many applications in engineering design, planning, scheduling, and marketing. However, MINLP models especially in engineering design results in complex engineering models which need special algorithms which are not computationally expensive, overly restrictive and mathematically intensive (Visnawathan & Grossmann, 1990). The algorithms for solving MINLP formulations can be classified into four main categories: Direct Linearization, Stochastic/Meta-heuristic Optimization, Deterministic Optimization, generation of a good starting point (Visnawathan & Grossmann, 1990; Quesada & Grossmann, 1995; Grossmann, 2014).

Direct Linearization

Within water network synthesis (WNS), for water minimisation, direct linearization entails the conversion of a nonlinear constraint to a linear constraint. Savelski & Bagajewicz, (2000, 2003) applied the necessary conditions of optimality for water minimisation in a water network by fixing the outlet concentration of the sinks at maximum and concentration of regeneration units at

minimum for all single contaminant cases. They also set outlet concentrations of key contaminants to be higher than all contaminants combined for a case involving multi-contaminants. They used these necessary conditions to attain direct linearization of mass-transfer-based-operations for water allocation problems.

The concept of Savelski & Bagajewicz, (2003) was applied by Walczyk & Jezowski, (2008) to directly linearize a water network problem. They did apply logical conditions to aid their solution, where water using operations parameters were selected among three heuristically selected conditions. Their technique, however, did not guarantee global optimality, although they reported to have gotten near global optimum solution with very short CPU times.

In cases where large scale problems are involved or mass-transfer-based operations with multi contaminants, direct linearization becomes a liability. Doyle & Smith (1997) presented a formulation for the modelling of mass-transfer-based problem, where the exact problem was used to get starting points for the solution of the exact problem. They presented the nonlinear fixed mass load model as the exact problem and fixed the outlet concentrations and solve it as a linear model. If the solution found is feasible, it could reduce significant computational time and near global optimality is increased. This method, however, can lead to elimination of important stream connections that could however lead to a better solution. Gunaratman et al. (2005) presents a linear relaxation of the water networking problem using sequential procedure to get a good starting point, or an iterative approach to determine a water network topology. They introduced slack variables to MILP formulations to cater for the mass lost and gained in mass transfer units. They used the flowrates obtained in the MILP for the LP formulations with the aim to minimise the slack and surplus variables in the formulation. The model is then solved iteratively, until a feasible solution is found. The solution obtained will then be used to initialise the exact MILP model. Just the other direct linearization techniques discussed above, global optimality is not guaranteed with this approach.

Stochastic/Meta-heuristic Optimisation

Stochastic or meta-heuristic optimization is a mathematical programming technique in which physical parameters are used to define random points that initiate a progression towards an equilibrium condition (Grossmann & Biegler, 2004; Grossmann, 2014). Handling uncertainty posed by data and parameters is a major challenge in addressing water network synthesis. There have been various approaches for optimization under uncertainty in the PSE domain, this includes scenario-based, two-stage and multistage stochastic programming (Dantzig, 2011), chance-constrained optimization (Gal & Nedoma, 1972), Flexible analysis (Grossmann & Sergeant, 1978), and Robust optimization (ElGhaoui & Lebret, 1997). However, there are only three applicable approaches that are considered when formulating optimization models for water network synthesis under uncertainty: (1) *Stochastic programming*, (2) *Robust optimization*, (3) *Stochastic optimal control* (Cheng, et al., 2004).

Within a stochastic programming formulation there is a specific methodology with two-stage model recourse that divides the decision variables into two stages called; “here-and-now” and “wait-and-see” variables (Birges & Louveaux, 1997). “Here-and-now” variables are those that have to be decided before future realization of uncertain parameters, whereas “wait-and-see” variables are used as correct measures or recourse against any infeasibilities arising during the unveiling of uncertainty (Birges & Louveaux, 1997). It can be said that second-stage variables help to accommodate any actual realization of uncertain parameters. In a water network synthesis problem under uncertainty, with two-stage structure, the maximum allowable water flows for reuse/recycle are determined in the first stage of design. As effects of uncertainty in the performance of the system is established in the second stage, operating decisions are made to meet the actually realized reuse/recycle in the sinks through modification of freshwater supply and wastewater flows (Khor, et al., 2014). The two-stage framework can be extended to a multistage paradigm to incorporate future recourse actions for multiperiod problems (Birge, 1997). Multiscenario two-stage stochastic programming suffers from the curse of dimensionality due to

an exponential increase in size with both numbers of scenarios and uncertain parameters (Khor, et al., 2014).

Robust Optimization has increasingly received attention in the past decade for addressing problems under uncertainty (ElGhaoui & Lebret, 1997). Originally, the approach of robust optimization assumes the uncertain parameters to be captured by ellipsoids (Ben-Tal & Nemirovski, 1998), while extensions are proposed to cover the continuous and discrete probability distributions (Li, et al., 2011). However, Khor et al. (2014) maintains that such representation of uncertainty can be a limitation for water network problems, whose random variables can be adequately described using finite set of known values from multiple discrete scenarios provided by historical data or expert experience.

Stochastic optimal control, sometimes referred to as Markov decisions process, uses a decision rule to describe a sequential decision-making problem that involves choosing an action in a certain state at a particular time (Khor, et al., 2014). While such a paradigm may fit the bi-level sequence of design and operation of water network problems, the approach is suitable for problems in which decisions are required on a real time basis. This is in contrast to a stochastic programming model, in which decisions are required to be taken less frequently due to the lower information level available regarding uncertainty.

Deterministic Optimization

Deterministic optimisation involves the use of global optimisation techniques such as branch and bound and cutting plane algorithms, which generally decompose MINLP problems to global optimal solutions. Quesada & Grossmann, (1995) presented an algorithm for optimisation of a water network problem using branch and bound techniques. They iterated both the exact and relaxed solution until optimum object function is found. Branch and Bound technique (BB) is an approximation where estimation is made to find feasible solution. Gupta & Ravindran (1985) and Nabar & Schrage (1990) proposed the BB algorithm for MINLP problems which is based on the same principles as LP based BB algorithm for MILP master problems (Quesada and Grossmann, 1995). Figure

2.21 illustrates the branch and bound framework, where P , is a non-convex problem and R , is the convex relaxation. The convex relaxation of the original problem is solved to attain a lower bound of the problem as presented in Figure 2.21a. Figure 2.21b presents the exact evaluation of the objective function within the feasible region, this is done to obtain the upper bounds of the global minimum. The relaxation gap shows the difference between the upper bound and lower bound and it relates to the degree to which the upper bound is close to global optimum.

In branch and bound framework, both the upper and lower bounds are adjusted iteratively until the relaxation gap is within a minimum tolerance. The value of the lower bound is constantly updated to divide the feasible region into finite number of sub-regions. Sub-regions that are proved not to contain the optimal solution are then systematically fathomed until an optimal solution is attained (Figure 2.21c). BB search tree algorithms works by solving the first problem that arises from the relaxation of the discrete conditions in the binary variables (Quesada & Grossmann, 1995). The procedure stops if the relaxation yields integral solution which is considered to be an optimal solution. However, if it does not yield an integral solution, the relaxed problem is used as a lower bound to the optimal solution, where a tree enumeration is performed and each node of the tree becomes a subset of the integrality condition. The integer solution that is found provides an upper bound to the solution, otherwise all the nodes that exceed the upper bound are eliminated and the search is continued until all nodes are understood (Figure 2.21d). BB approach for MINLP problems have a disadvantage since the resulting nodes in the tree are NLP sub-problems that cannot be easily updated (Quesada and Grossmann, 1995). Also the size of the problems can be significantly large since they are formulated in both continuous and binary space. The upper and lower bounds and quality of the convex relaxation determines the computational time required for a branch and bound framework.

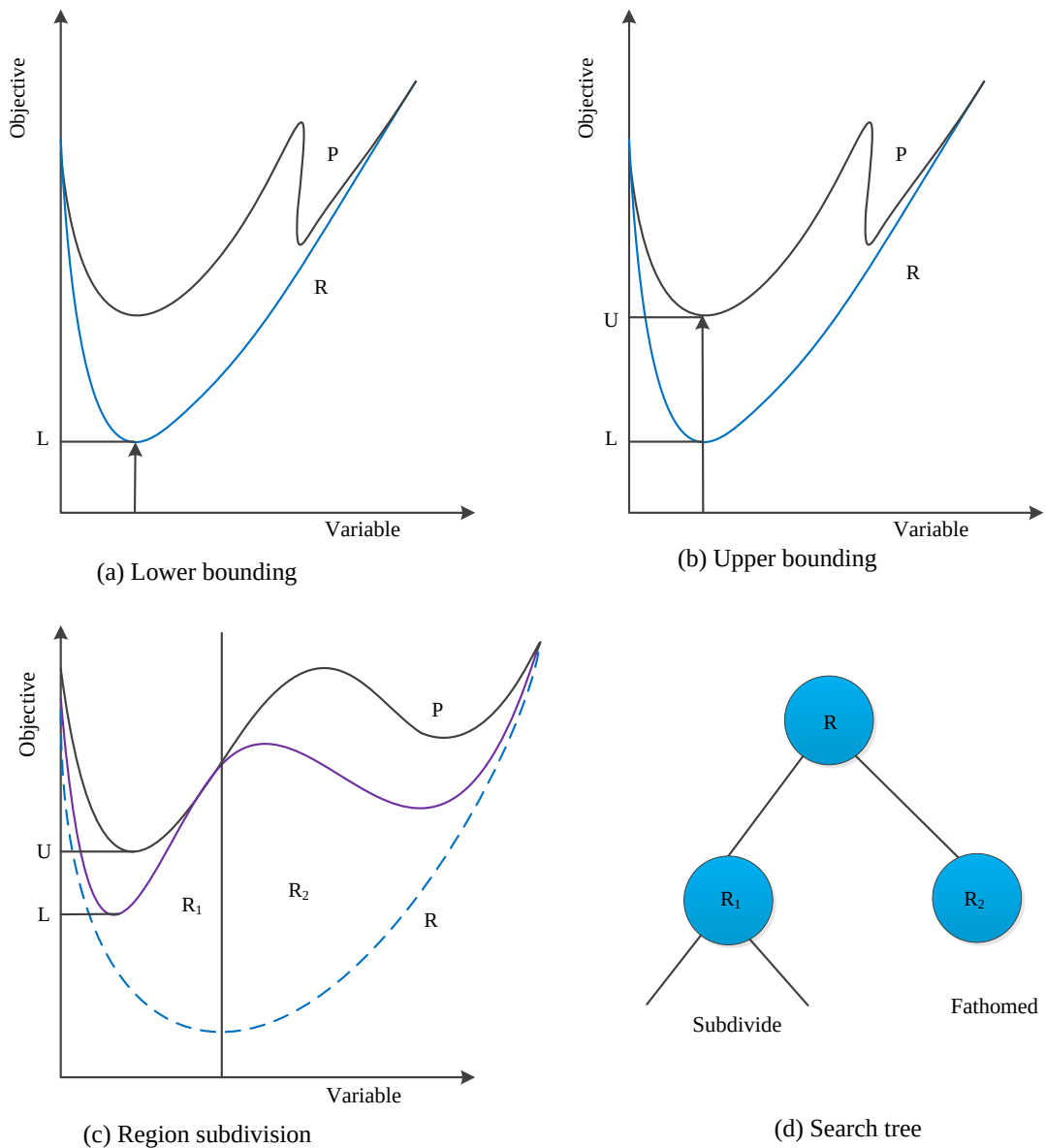


Figure 2.21: Spatial branch and bound procedure (Ryoo & Sahinidis, 1995)

Feasibility-based or optimality-based range reduction techniques are normally employed to contract the bounds. Feasibility-based techniques eliminate parts of the nonconvex problem that would be infeasible by using the structure of the constraints and the variable bounds iteratively. Optimality-based techniques use convex relaxation to eliminate regions where the objective function will be higher than the upper bound (Zamora & Grossmann, 1998). Application of feasibility-

based or optimality-based range reduction techniques results in the global solver branch and reduce optimisation navigator (BARON). BARON is one of the solvers that set to guarantee global optimality for MINLP problems.

Cutting plane Method. The cutting plane method is a mathematical optimization technique which is used to iteratively refine a feasible set by means of linear inequalities termed cuts (Duran & Grossmann, 1986). The cutting plane method is used to find integer solutions for MILP problems.

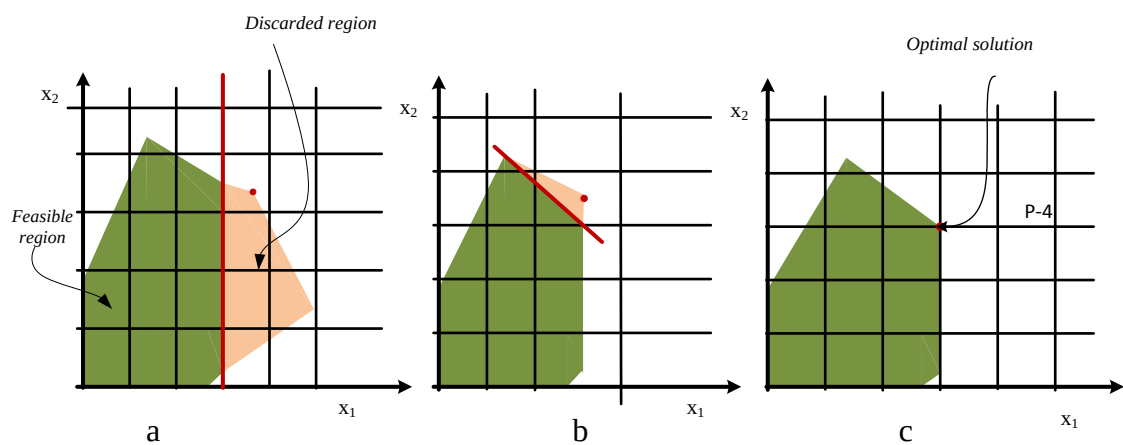


Figure 2.22: The cutting plane techniques (Kelly, 1960)

The method works by solving linear relaxation of the integer problem such that if the relaxed solution is found to be an integer solution the algorithm terminates, otherwise, there is guaranteed to exist a linear inequality that separates the optimum from the convex hull of the true feasible set. Successive cuts are made until an integer solution is found (Kelly, 1960) as illustrated in Figure 2.22.

The cutting plane method guarantees global optimality of convex inequality constraints and linear inequality constraints and objective functions (Pörn, et al., 1999). Figure 2.22a, shows a convex region of feasible solutions defined by several constraints. The grid indicates where the feasible integer solution lies; the dot represents the optimal solution for the relaxed solution. If the solution of the relaxed solution in Figure 2.22a is not integer solution, a section of the polygon is

cut again to find an integer solution (Figure 2.22b). The iteration does not stop and continuous repeatedly until an integer solution is found (Figure 2.22c).

The GBD algorithms divides variables into a set of complicating and non-complicating variables within an MINLP framework, the binary variables are usually considered the complicating variables (Quesada & Grossmann, 1995; Geoffrion, 1972). The GBD algorithm starts by solving a sequence of NLP subproblems and MILP master problems within the space of the complicating variables. The solution of the subproblem generates an upper bound to the optimal solution of the MINLP problem. The GBD algorithms offers an advantage where special structures in the NLP subproblem can easily be exploited, however it requires a significant amount of major iterations to solve NLP subproblems and MILP master problems to solved successfully (Visnawathan & Grossmann, 1990).

The ECP algorithm is an extended method of Kelly's CP method for solving nonconvex MINLP problems. The procedure does not provide new perspective in the solution of MINLP problems (Westerlund & Pettersson, 1995). The ECP procedure requires a single MILP solution in each iteration step. The solution algorithm is however suited for large convex MINLP problems with unrestrained degree of nonlinearity. Furthermore the ECP algorithm does not solve NLP subproblems separately. Other notable algorithms for solving MINLP problems are the feasibility technique. The feasibility technique is not computationally expensive since it is based on the principle of finding feasible integer points that has the smallest local degradation with respect to the relaxed NLP solution (Visnawathan & Grossmann, 1990). It does however have a disadvantage of not being able to guarantee optimality. Cutting plane method also have a problem of using parallel algorithm for matrix multiplication and in practice takes a longer period of time to solve.

Outer approximation algorithms. This was initially proposed by Duran and Grossmann (1986) to deal with MILP and NLP problems. This was later extended by Viswanathan and Grossmann (1990) to cater for the more complex MINLP problems. They developed a new outer approximation and equality relaxation OA/ER algorithm with a new master MILP master plan that includes an exact

penalty function that allows for the violation of the linearization of nonlinear functions. The algorithms starts with the solution of the relaxed NLP problem hence do not require specification of initial 0 – 1 variables (Visnawathan & Grossmann, 1990). OA/ER does not guarantee convergence to global optimum; however, it has proven to be computationally efficient, robust and reliable in many problems.

Generation of a Good Starting Point

Furthermore, another way to get away with nonlinearity in a mathematical model is get a good initial point so that the solution technique may start with it. To get an initial point is to solve a relaxed model of the original problem and the solution you get becomes the initial starting point. However, if the original problem is linearized then the LP model can be solved without needing an initial starting point. Generation of a good starting point is usually adopted and applied in mass-transfer based problems to fix process outlet concentrations to maximum values (Teles, et al., 2008). Within water minimisation frame work, initial guesses are adopted for wastewater treatment network by (Li & Cheng, 2007) . Teles, et al., (2008) presented an approach for optimal water-using networks by replacing a nonlinear program (NLP) with a succession of linear programs (LP) by generating different substructures of the overall superstructure and solve independently. The approach generates different starting points for the NLP problem by decomposition of the main superstructure into sub-structures. The work of Teles et al., (2008) when compared to standard initialization procedure with a single starting point proved efficient, however, it proved to be computationally intensive.

Glover, (1975) Proposed a method of removing non-linearities in a model due to the product of binary variable and continuous variable. Assuming a function

$$xy = F \quad (2.1)$$

Where x is continuous variable and y is a binary variable. Equations (2.2) to (2.4) are linear in terms of the product of xy based on the Glover transformation procedure.

$$X^L \leq x \leq X^U \quad (2.2)$$

$$X^L y \leq \Gamma \leq X^U y \quad (2.3)$$

$$x - X^U(1-y) \leq \Gamma \leq x + X^L(1-y) \quad (2.4)$$

However, equations (3) and (4) are added to the existing equations which are one of the effective ways of removing non-linear terms arising due to the product of continuous and binary variables. This is an exact transformation technique for the non-linear term xy , which will not interfere with finding a globally optimal solution in a model provided the remainder of the formulation is linear (Glover, 1975).

Another method to handle bilinearity involving the product of two continuous variables is the Reformulation – Linearization technique (Sherali & Alameddine, 1992) which was based on the concave over and under estimator by (McCormick, 1976) as discussed by Quesada & Grossmann (1995). This technique does not offer direct linearization technique and does not always guarantee feasibility. Quesada & Grossmann (1995) however, embedded the reformulation-linearization technique inside branch and bound procedure in order to obtain global optimal solution. Consider a product of two continuous variables as shown in constraint

$$xy = \Gamma \quad (2.5)$$

In this regard the McCormick underestimators and overestimators for a linear term in (2.5) are illustrated by constraints (2.6) to (2.9). The superscript L and U represents the lower and upper bounds of the respective terms.

$$\Gamma \geq xY^U + X^U y - X^U Y^U \quad (2.6)$$

$$\Gamma \geq xY^U + X^L y - X^L Y^L \quad (2.7)$$

$$\Gamma \leq xY^U + X^L y - X^L Y^U \quad (2.8)$$

$$\Gamma \leq xY^L + X^U y - X^U Y^L \quad (2.9)$$

Quesada & Grossmann (1995) confirmed that this is not an exact linearization technique, although it does create a convex solution space. The technique also creates an over-estimation and under estimating envelope around the nonlinearity which does not require an initial starting point. In this technique, if both the linearized model and non-linear model show exact solution, then the solution is considered to be globally optimal. However if the models do not show exact solutions then global optimality cannot be guaranteed.

2.7 Conclusion

This Chapter gives a comprehensive review on the optimization of water networks (WN). Background is given on the synthesis of membrane regeneration units within water networks including the “black-box” representation. Both graphical and mathematical methods for water network synthesis and optimization have been discussed, especially regarding huge problems involving multi-contaminants. The challenges faced in solving mixed-integer nonlinear programming (MINLP) models have been discussed with available algorithms highlighted. The chapter also highlights the different approaches that have been used over the years to solve problems involving MINLP or NLP problems within water network synthesis problems.

From the discussions, it is clear that there still exist gaps in determining accurate representation of water networks. Chapter 3 therefore presents a robust mathematical model of a water network including detail models of both ED and RO units to capture the design features of the units for simultaneous water and energy minimization.

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CHAPTER 3

MODEL DEVELOPMENT

3.1 Introduction

This chapter entails the development of the optimization model for water and energy minimisation. Firstly, a water network superstructure (WNS) is designed based on the problem statement in chapter 1. A mathematical model is then formulated using the designed superstructure based on the source-regeneration-sink framework. A detailed mechanistic model of the membrane regeneration units (ED and RO) will be conducted to allow for the synthesis of the regeneration units to obtain optimal design parameters and total annualised costs (TAC) considering the operating and capital costs of the membrane regeneration units. Finally, the detailed mechanistic models of both ED and RO regenerators will be incorporated into the overall objective function of the water network superstructure.

3.2 Water Network Superstructure

Based on the problem statement in chapter 1, a WNS in Figure 3.1 is developed. The superstructure representation is an extension of the work by Khor et al. (2011). The superstructure in this work incorporates multiple regenerators which are open for parallel and series connection as well as recycle and reuse of both permeate and reject streams from regenerators. The fixed flowrate approach adopted in this work considers water using processes as sources and sinks that generate or consume a fixed amount of water respectively. This is done by setting

fixed contaminant concentrations for sources and variable contaminants for sinks bounded by permissible upper bounds (Poplewski, et al., 2010). Total fixed flowrate is adopted because it presents a general representation of both mass transfer and non-mass transfer-based water using operations (Khor, et al., 2012).

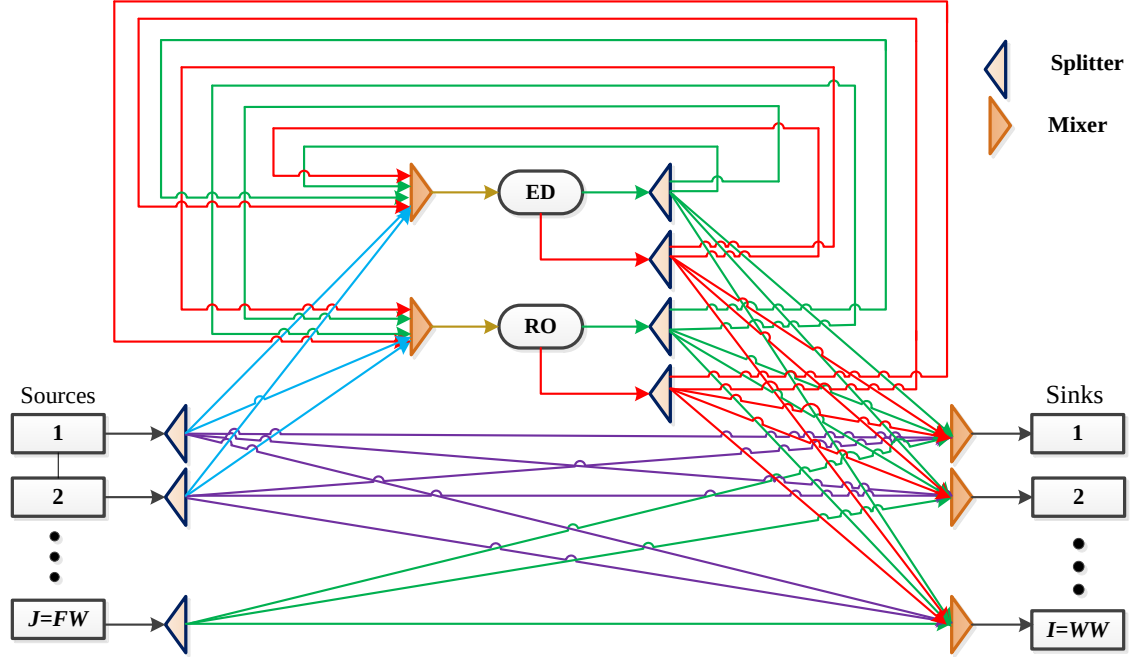


Figure 3.1: General water network superstructure with multiple membrane regenerators

3.3 Water Balances

Water balance formulations are conducted to establish the source-regenerator-sink connectivity based on Figure 3.1.

3.3.1 Mass Balances for Sources

Figure 3.2 shows a schematic representation of water sources, $j \in J$, water recycle and reuse streams within the membrane regeneration units, and water sink i , that receives water from sources, and both permeate and reject stream of the membrane regeneration units. Based on Figure 3.2, the flowrate, Q_j^x from any source, j , can split into different streams for direct reuse/recycle or for

regeneration. The corresponding material balance is shown in constraint (3.1). Where, $Q_{j,i}^a$ is the flowrate from any particular source, j to sink, i , Q_j^{ed} and Q_j^{ro} are flowrates from source to the ED and RO regenerators respectively.

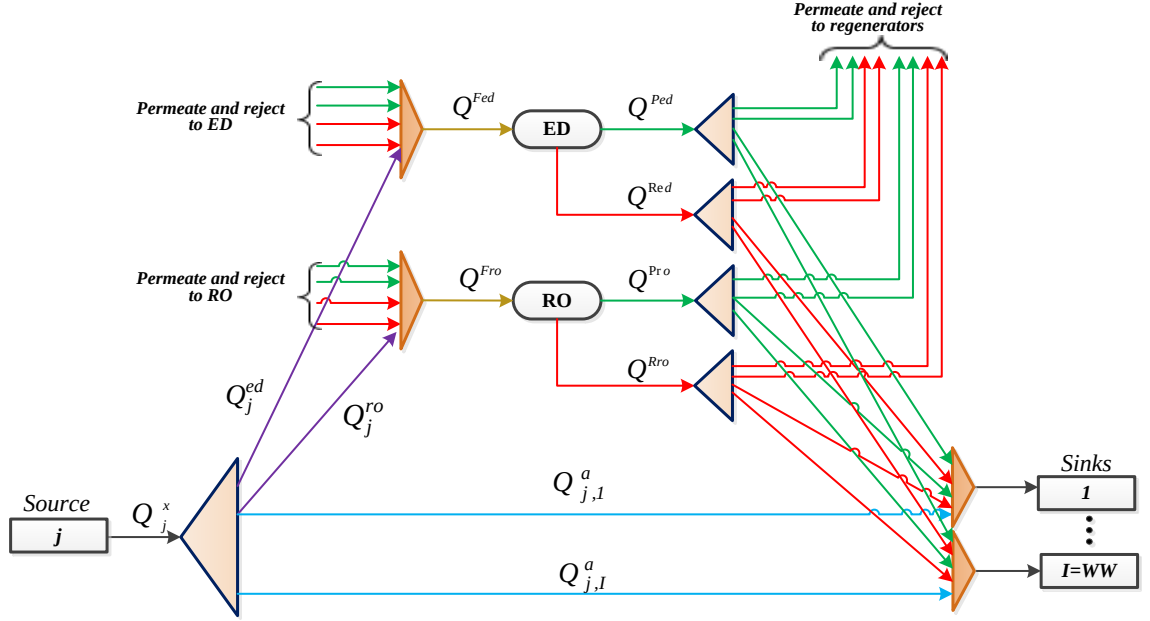


Figure 3.2: Schematic representations of source-sink-regenerators

$$Q_j^x = \sum_{i \in I} Q_{j,i}^a + Q_j^{ro} + Q_j^{ed} \quad \forall j \in J \quad (3.1)$$

It should be noted that the wastewater sink, WW, is considered as the final sink

3.3.2 Mass and Concentration Balances for Regeneration Units

Figure 3.3 gives a schematic representation of water recycle and reuse within the membrane regeneration units.

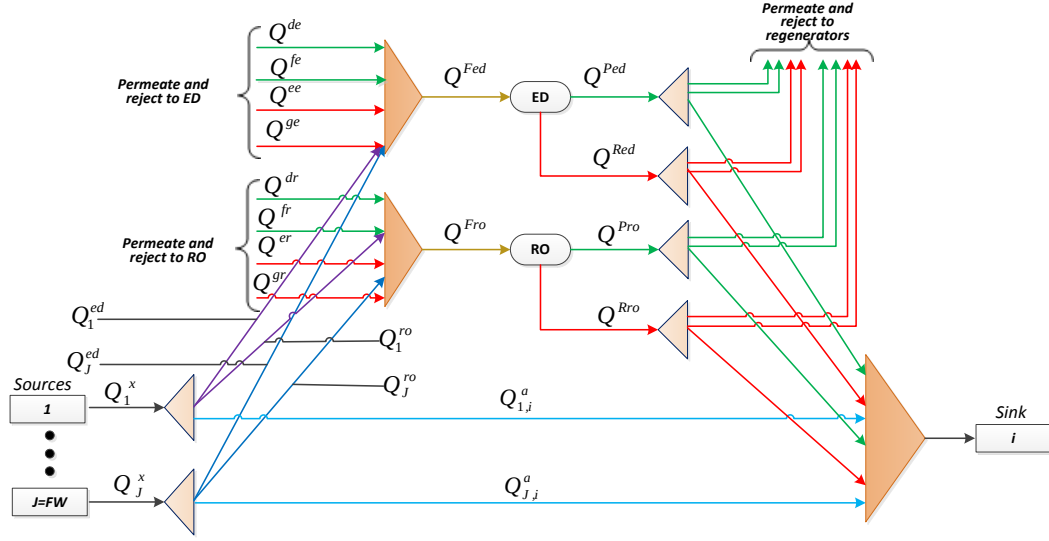


Figure 3.3: Schematic representation of regeneration network

Flow and load balances are conducted for all streams entering the regenerator units. The streams from sources, permeate, and reject streams of both regenerators, are open to reuse/recycle depending on the component concentration limits of the regeneration units. Constraints (3.2) and (3.3) are water balances around the mixer preceding the ED and RO units respectively. Where Q^{Fro} and Q^{Fed} are the total flowrates into the ED and RO units respectively. Here Q^{dr} and Q^{er} , is permeate and reject flowrates from the ED unit into the RO unit. Whereas, Q^{fr} and Q^{gr} , are permeate and reject flowrates from the RO unit into the RO unit.

$$Q^{Fro} = \sum_{j \in J} Q_j^{ro} + Q^{dr} + Q^{er} + Q^{fr} + Q^{gr} \quad (3.2)$$

$$Q^{Fed} = \sum_{j \in J} Q_j^{ed} + Q^{de} + Q^{ee} + Q^{fe} + Q^{ge} \quad (3.3)$$

Similarly, Q^{de} and Q^{ee} , Q^{fe} and Q^{ge} are flowrates from permeate and reject streams of ED and RO units into the ED unit.

On the basis of the varying tolerance of contaminants of the ED and RO units, a contaminant balance for the regenerator feed is conducted based on the maximum contaminant each regenerator can take. Hence the corresponding contaminant

balance around the mixer of each regenerator unit is represented by constraints (3.4) and (3.5) for ED and RO respectively.

$$C_{co}^{Ue} \geq \frac{\sum_{j \in J} Q_j^{ed} C_{j,co}^x + Q^{de} C_{co}^{Ped} + Q^{ee} C_{co}^{Red} + Q^{fe} C_{co}^{Pro} + Q^{ge} C_{co}^{Rro}}{Q^{Fed}} \quad \forall co \in CO \quad (3.4)$$

$$C_{co}^{Ur} \geq \frac{\sum_{j \in J} Q_j^{ro} C_{j,co}^x + Q^{dr} C_{co}^{Ped} + Q^{er} C_{co}^{Red} + Q^{fr} C_{co}^{Pro} + Q^{gr} C_{co}^{Rro}}{Q^{Fro}} \quad \forall co \in CO \quad (3.5)$$

It should be noted that, C_{co}^{Ue} and C_{co}^{Ur} are the maximum allowable contaminants into the ED and RO units respectively. Where $C_{j,co}^x$ is the concentration of contaminant, co , from any source j . Whereas C_{co}^{Ped} and C_{co}^{Red} , C_{co}^{Pro} and C_{co}^{Rro} are concentrations of contaminant, co , for both permeate and reject stream of ED and RO units.

3.3.3 Mass and Concentration Balances for Permeate and Reject Streams

Figure 3.4 shows a schematic of permeate and reject stream from the ED regenerator unit that splits into sinks, recycle into the ED unit and RO unit.

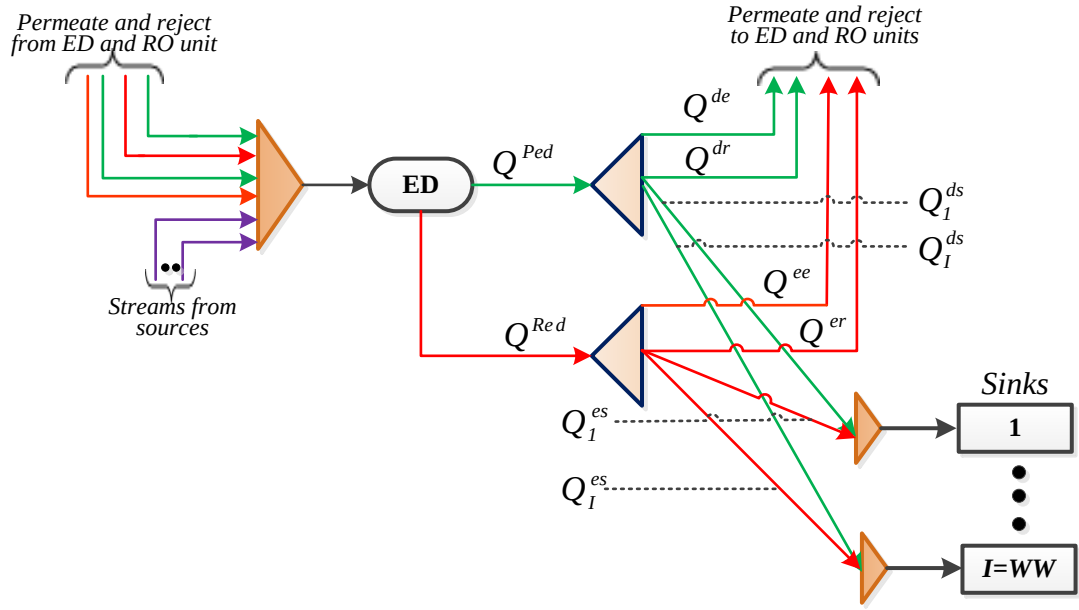


Figure 3.4: Schematic representation of permeate and reject stream of regeneration unit

Based on Figure 3.5, water balances for permeate and reject streams of the ED unit are represented in constraints (3.6) and (3.7). The flowrates from permeate and reject streams into sinks are represented by Q_i^{ds} and Q_i^{es} .

$$Q^{Ped} = \sum_{i \in I} Q_i^{ds} + Q^{dr} + Q^{de} \quad (3.6)$$

$$Q^{Red} = \sum_{i \in I} Q_i^{es} + Q^{er} + Q^{ee} \quad (3.7)$$

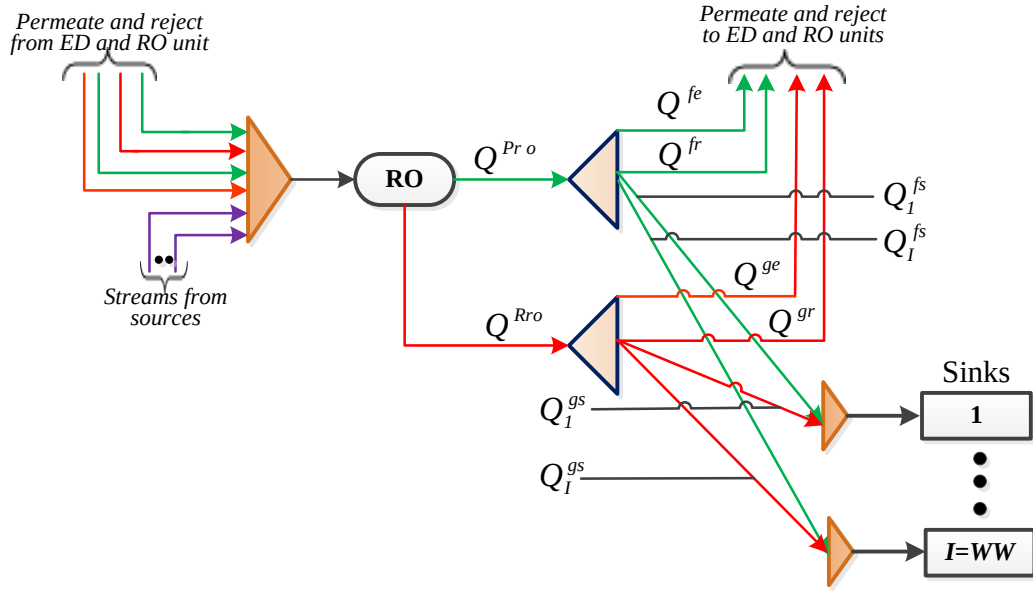


Figure 3.5: Schematic representation of permeate stream

Similarly, the water balances for permeate and reject streams of the RO unit are represented by constraints (3.8) and (3.9). Where Q_i^{fs} and Q_i^{gs} are permeate and reject flowrates into sinks.

$$Q^{Pro} = \sum_{i \in I} Q_i^{fs} + Q^{fr} + Q^{fe} \quad (3.8)$$

$$Q^{Rro} = \sum_{i \in I} Q_i^{gs} + Q^{gr} + Q^{ge} \quad (3.9)$$

3.3.4 Mass and Concentration Balances for Sinks

Figure 3.6 is a schematic representation of water sink that receives water from sources and both permeate and reject stream of the membrane regenerators. The water balances into a particular sink is represented by constraint (3.10). The parameter Q_i^z is the maximum flowrate into a particular sink i .

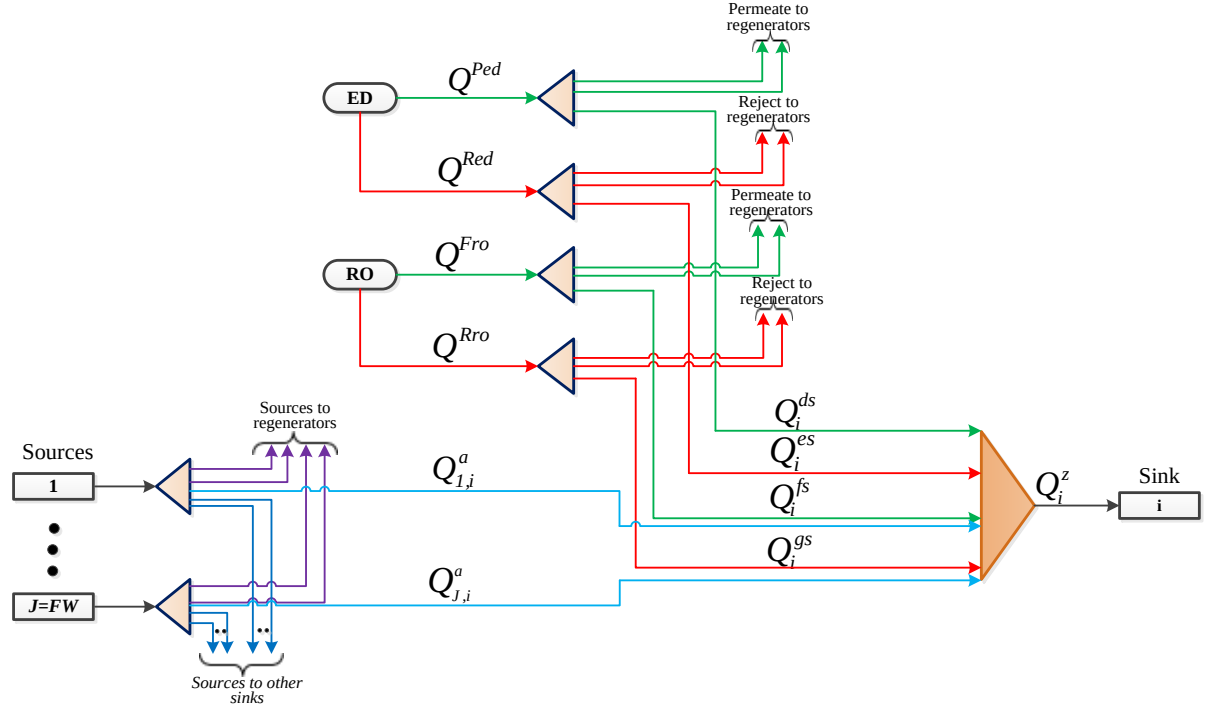


Figure 3.6: Schematic representation of a water sink

$$\sum_{j \in J} Q_{j,i}^a + Q_i^{ds} + Q_i^{es} + Q_i^{fs} + Q_i^{gs} = Q_i^z \quad \forall i \in I \quad (3.10)$$

It should be noted, however, that the last source represents the freshwater source, FW. The maximum load into any sink, i , should not exceed the maximum allowable contaminant concentrations $C_{i,co}^U$, into that sink. This constraint is expressed by constraint (3.11).

$$\frac{\sum_{j \in J} Q_{j,i}^a C_{j,co}^x + Q_i^{ds} C_{co}^{Ped} + Q_i^{es} C_{co}^{Red} + Q_i^{fs} C_{co}^{Pro} + Q_i^{gs} C_{co}^{Rro}}{Q_i^z} \leq C_{i,co}^U \quad \forall co \in CO \quad \forall i \in I \quad (3.11)$$

3.4 Design of ED Model

This section presents a detailed mechanistic model of a single stage electrodialysis regeneration unit based on the work of Tsiakis and Papageorgiou, (2005). Figure 3.7 is a single stage ED unit considered to demonstrate the interaction between the

water network and the regeneration unit and also to enhance simplicity of the formulation.

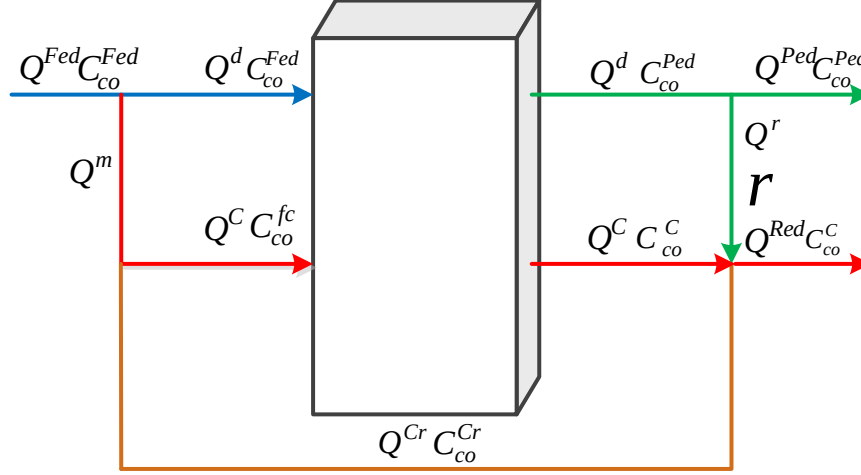


Figure 3.7: Schematic of a single stage ED plant

In order to formulate the model for the regeneration unit, assumptions are made to describe the feed solution properties, hardware dimensions and operating conditions (Lee et al., 2002).

The assumptions are:

- (i) The diluate and concentrate cells are geometrically similar with identical flow patterns.
- (ii) The flowrate in the diluate and concentrate compartments are equal and uniform $Q^d = Q^c$.
- (iii) The fluid considered is Newtonian, i.e. the viscosity remains constant.
- (iv) The unit is operated in a co-current flow.
- (v) During operation the current should not exceed the limiting current density
- (vi) Water transport across the membrane is negligible compared to the flowrate in the diluate and concentrate streams.
- (vii) Membrane thickness is negligible.

- (viii) The concentration of the salt species is calculated using molar equivalents.

From the diagram Q^d is the diluate flowrate, Q^c is the concentrate stream flowrate, Q^{cr} is the concentrate stream recycle flowrate, Q^m is the flowrate from the feed stream that mixed with the concentrate stream to balance the flowrates. Whereas, C_{co}^{fc} is the feed concentration for the concentrate stream.

Physical parameters and necessary variables are incorporated to obtain an MINLP model. The total annualised cost TAC_e , comprises of the electric current through the ED unit, stack design considerations, desalination energy requirement, pumping energy requirement and material balances and is formulated based on the following constraints.

Electric Current

The required electrical power through an ED unit is based on Faraday's law which relates to the driving force that is required to transfer electrons from one stream to another in the ED unit as related in Lee, et al. (2002). It also relates to the degree of desalination, C_{co}^A , the flowrate of the diluate stream and the number of cell pairs N in the stack as represented in constraint (3.12). ζ , is the current utilisation, F is the faraday's constant which is required for the total current required to drive electrons from one stream to the other. The electrochemical valences of the ionic contaminants are represented by z .

$$I = \frac{Q^d F C_{co}^A z}{\zeta N} \quad (3.12)$$

The degree of desalination is measured by the concentration difference between the diluate and concentrate streams across the ED unit as defined by the mass balance in constraint (3.13).

$$C_{co}^A = C_{co}^{Fed} - C_{co}^{Ped} = C_{co}^C - C_{co}^{fc} \quad (3.13)$$

The limiting current density is determined by the mass transfer coefficient for the transport of ions across the membrane surface. This is difficult to determine theoretically, since it is a function of solution flow velocity, concentration and stack and spacer configuration (Lee, et al., 2002). Therefore, the limiting current density is determined experimentally for a certain flow velocity, concentration and stack configuration as shown in constrain (3.14).

$$I^{prac} = \varepsilon a^{LCD} C_{co}^d(u)^{b^{LCD}} \quad (3.14)$$

A safety factor, ε , within the range of 0.7 to 0.9, is used to adjust the practical limiting current density which is dependent on the flow pattern. Constants a and b are determined by measuring the limiting current density under different flow conditions.

Stack Design Considerations

Efficient operation of an ED unit is dependent on the membrane area for a given feed solution, current density, number of cell pairs as well as the production rate (Tsiakis & Papageorgiou, 2005). Spacers are used to enhance mixing and attain uniform flow through the ED unit and also to separate and support the membranes. However, they reduce the volume of available cell, hence decreasing the flowrate. A safety factor, α , is included to cater for the corrections as shown in constraint (3.15). Here δ , is the cell thickness, w is the diluate cell width and v is the linear flow velocity.

$$Q^{Ped} = N w \delta u \alpha \quad (3.15)$$

Membrane area is one of the design characteristics that determine the rate of desalination within an ED unit. The rate of desalination increases with the exposure of feed water on the membrane area. The presence of spacers reduces the available area for current due to shadow effect. As a result the practically required membrane area is larger than the theoretically required area. A correction factor, β , is introduced to account for this effect as can be seen in constraint (3.16).

$$A = \frac{\left[\ln \frac{C_{co}^C C_{co}^{Fed}}{C_{co}^{Ped} C_{co}^{fc}} + \frac{\Lambda \rho^{AC} C^{\Delta}}{\delta} \right] C_{co}^{Ped} Q^d zF}{\left[\frac{C_{co}^{Ped}}{C_{co}^{Ped}} + 1 + \frac{\Lambda C^d}{\delta} \rho^{AC} \right] I^{prac} \beta \zeta} \quad (3.16)$$

From constraint (3.16), the parameter ρ^{AC} is the area resistance of the anion and cation exchange membranes, Λ is the equivalent electrical conductivity of the solution.

Energy Requirement

The energy required for the operation of an ED system is made of two components. The energy required for the transfer of ions from the solution across membrane material and the energy required for pumping the feed solution through the ED unit. The rate of consumption of either form of energy is dependent, among other factors, on the concentration of feed solution and the available membrane area to the feed solution.

Direct energy required in an ED unit is dependent on the voltage and current applied across the unit. The voltage drop across an ED unit is a result of resistance and potentials due to solutions of different salt concentration (Strathmann, et al., 1997). The resistance is as a result of friction between ions with membrane matrix and water molecules. There is also energy loss due to electrode processes in the terminal compartments, although the energy loss due to resistance is much greater. It is, therefore, advisable to use membranes with low electrical resistance. Membranes should be closely arranged in order to reduce energy losses due to resistance of the cell pair unit as a result of salt transfer (Strathmann, et al., 1997). Based on Ohm's law, the voltage U , applied across an ED unit is shown in constraint (3.17).

$$U = \frac{C^{\Delta} N Q^d zF}{\zeta A} \left[\frac{\delta \ln \frac{C_{co}^C C_{co}^{Fed}}{C_{co}^{Ped} C_{co}^{fc}}}{\Lambda C_{co}^{\Delta}} + \rho^{AC} \right] \quad (3.17)$$

The voltage across an ED unit is, therefore, related to the total power, P_{ower} , required to produce a product capacity, Q^{Ped} . The specific energy required for desalination is represented by constraint (3.18).

$$P_{ower} = UI \quad (3.18)$$

$$E_{spec} = \frac{P_{ower}}{Q^{Ped}} \quad (3.19)$$

The pumping energy is the energy consumed in pumping the feed water into the ED unit. Since the membrane compartment is arranged in a rectangular form, the flows through the diluate and concentrate streams are considered to be passing through a rectangular channel. The geometry of the pipe is considered to be that of rectangular channel with a pressure drop ΔP , considered to be of a laminar flow as represented by constraint (3.20), which is a modified Hagen-Poiseuille equation for this type of geometry. The symbol μ is the viscosity of water, d is the diameter of the rectangular channel of the ED unit, L is the process path length of the ED unit.

$$\Delta P = \frac{12V \mu L}{d^2} \quad (3.20)$$

The pumping energy is, therefore, calculated based on the pressure drop as shown in constraint (3.21). Here Γ is a conversion factor available in literature, η_p is the pumping efficiency (Tsiakis & Papageorgiou, 2005).

$$E_{pump} = \frac{\Delta P K^{\Gamma}}{\eta_p} \quad (3.21)$$

Material Balances

Material balances are conducted around the ED unit in Figure 6 in order to conserve mass by accounting for materials entering, leaving or mixing within the unit as shown in constraints (3.22) to (3.26).

$$Q^{Fed} = Q^{Ped} + Q^{Red} \quad (3.22)$$

$$Q^{Fed} = Q^d + Q^m \quad (3.23)$$

$$Q^d = Q^{Ped} + Q^r \quad (3.24)$$

$$Q^c = Q^m + Q^{cr} \quad (3.25)$$

$$Q^{Red} = Q^c + Q^r - Q^{cr} \quad (3.26)$$

Corresponding load balances are conducted across the ED unit in order to obtain the species balance in the streams and to demonstrate that the amount of contaminants removed from the diluate stream equals the amount of contaminants accumulated in the concentrate stream, for the case where $Q^c = Q^d$.

$$Q^{Fed} C_{co}^{Fed} = Q^{Ped} C_{co}^{Ped} + Q^{Red} C_{co}^{Red} \quad \forall co \in CO \quad (3.27)$$

$$Q^r C_{co}^{Ped} + Q^c C_{co}^C = Q^{cr} C_{co}^{Cr} + Q^{Red} C_{co}^{Red} \quad \forall co \in CO \quad (3.28)$$

$$Q^m C_{co}^{Fed} + Q^{cr} C_{co}^{Cr} = Q^c C_{co}^{fc} \quad \forall co \in CO \quad (3.29)$$

$$Q^d C_{co}^{Fed} + Q^c C_{co}^{fc} = Q^d C_{co}^{Ped} + Q^c C_{co}^C \quad \forall co \in CO \quad (3.30)$$

The liquid recovery rate, r , is the amount of product water that is directed to the recycle concentrate stream in order to reduce its salinity and is shown in constraint (3.31). It is required in order to avoid water transport due to osmosis across the membranes (Tsiakis & Papageorgiou, 2005).

$$r = \frac{Q^{Ped}}{Q^d} \quad (3.31)$$

The purge concentrate is replaced by an amount of the less concentrated feed, and is represented by the mixing ratio, m , in constraint (3.32).

$$m = \frac{Q^d}{Q^{Fed}} \quad (3.32)$$

Based on the formulation and physical design of the ED unit it is assumed that both the diluate and concentrate maintain a constant flowrate. This is done in order to avoid strain on the membrane material.

The cost function of the ED regeneration unit which is expressed as the TAC_e comprises of the capital and operational costs. The capital cost consists of the costs associated with the purchase of pumping equipment, and the establishment of the plant. The operating cost is the costs incurred due to day to day running of the plant over a specified time. It is associated with the electrical energy costs due to pumping of feed water into the system and desalination. Both costs are incorporated into a single function called TAC_e which is synthesised to obtain optimal design parameters as shown in constraint (3.33). Here K^{mb} is the capital cost of membrane, t^{max} is the maximum equipment life, AOT is the annual operating time of the plant, K^{el} represents the cost of the electrical power.

$$TAC_e = \frac{K^{mb} A}{t^{max}} + AOT K^{el} Q^{Ped} [E^{Pump} + E^{spec}] \quad (3.33)$$

3.5 Design of RO Model

Figure 3.8 is a schematic representation of a reverse osmosis membrane regeneration unit based on the works of El-Halwagi (1997) and Khor et al. (2011). Detailed synthesis of the membrane regeneration unit is conducted to obtain optimal design parameters based on number of membrane modules, feed flowrates and energy required for pumping. In industrial applications, reverse-osmosis

networks (RON) are used for the separation processes. A RON comprises of multiple RO modules, pumps, and turbines to form a system. The task of this section is to formulate a mathematical model of a hollow-fibre RON based on El-Halwagi (1997). The formulated model is synthesised based on the pumps, reverse-osmosis modules and energy recovery turbines from the high pressure reject side (Khor, et al., 2012)

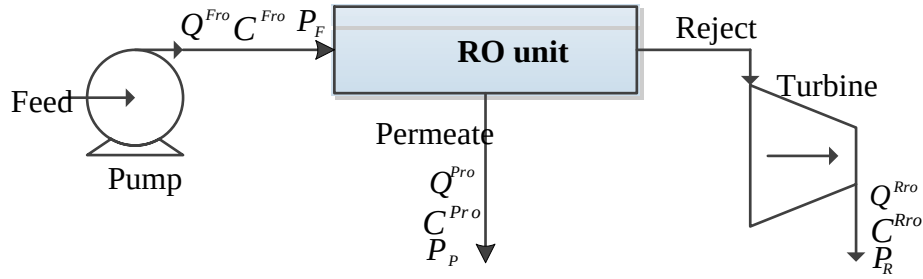


Figure 3.8: Schematic of a reverse osmosis unit

In modelling a RON there are two main considerations, such as, membrane transport equations and the hydrodynamic modelling of the RON modules. The membrane equations have to do with water permeation and solute flux taking place at the membrane surface. Hydrodynamic modelling deals with microscopic transport of various species along with the momentum and energy associated with it. The separation efficiency of a RON is dependent on the influent solute concentration, pressure and water flowrate (Yang, et al., 2014).

Membrane Transport Equations

Transport equations are used to predict the flux of water and solute based on the work of Dandavati *et al.* (1975) and Evangelista (1986). Both the water and solute flux equations are valid for all reverse osmosis module configurations. The solute flux, N_{solute} , relates to the transport of solute by diffusion due to the transport of water across the membrane phase and is given by constraint (34). Where $\left[\frac{D_{2M}}{K\delta} \right]$

the solute is flux constant and C_s is the average concentration on the feed side of the RO unit.

$$N_{solute} = \left[\frac{D_{2M}}{K\delta} \right] C_s \quad (3.34)$$

Water flux relates to rate at which water permeates through RO unit. It is directly related to the temperature and pressure as well as RO module dimensions and water properties as shown in constraint (3.35). Here A_p is the water permeability constant, ΔP is the pressure drop across the unit, π_F is the osmotic pressure on the feed side of the RO unit, and γ is a constant that represents the design features of the hollow fibre module.

$$N_{water} = A_p \left[\Delta P - \frac{\pi_F}{C_{co}^{Fed}} C_s \right] \gamma \quad \forall co \in CO \quad (3.35)$$

Average Shell Side Concentration

The average concentration on the shell side of the membrane is the average of the feed and rejects concentration as represented in constraint (3.36).

$$C_s = \frac{C_{co}^{Fro} + C_{co}^{Rro}}{2} \quad \forall co \in CO \quad (3.36)$$

Trans-Membrane Pressure

The pressure drop across the membrane is the difference in pressure between the feed side and the permeate side of the membrane unit. It is the driving force for membrane performance and product water production. The pressure difference across a RON increases with increasing flux across the membrane which is represented by constraint (37). Here P_F , P_R and P_p are the feed, retentate and permeate pressures of the RO unit respectively.

$$\Delta P = \frac{P_F - P_R}{2} - P_p \quad (3.37)$$

The pressure on the shell side ΔP_{shell} , of the RO hollow-fibre module is represented by the pressure difference between the feed side and the reject side of the RO unit.

$$\Delta P_{shell} = P_F - P_R \quad (3.38)$$

Substituting the shell side pressure drop into the pressure drop across the reverse osmosis unit gives rise to the feed pressure applied to the RON.

$$P_F = \Delta P + \left[\frac{\Delta P_{shell}}{2} + P_p \right] \quad (3.39)$$

Power Across the RON

The power of turbine and pump across RON is represented by constraints (3.40) and (3.41) respectively. Here P_{atm} is the atmospheric pressure and ρ is the density of water.

$$Pow_{(turb)} = \frac{Q^{Rro} [P_R - P_{atm}]}{\rho} \quad (3.40)$$

$$Pow_{(pump)} = \frac{Q^{Fro} [P_F - P_{atm}]}{\rho} \quad (3.41)$$

Average Concentration on the Feed Side

The osmotic pressure on the feed side of RON is a function of the contaminant concentration (El-Halwagi, 1997). In this formulation the osmotic pressure on the permeate side is neglected since the concentration is assumed to be significantly lower. The osmotic pressure on the retentate side $\Delta \pi_{ro}$ is adopted from the formulation of Saif, et al. (2008) and is shown in constraint (3.42).

$$\Delta \pi_{ro} = OS \sum_{co \in CO} C_{co}^{Fro} \quad (3.42)$$

The osmotic pressure coefficient OS , ranges between osmotic pressure on the feed side and average solute concentration on the feed side. The average concentration on the feed side (constraint 43) is reformulated based on the concentration on the permeate side as adopted from Khor, et al. (2011). The pressures across the membrane material and membrane area are important parameters that determine the performance of the RON. Where S_c is the solute permeability coefficient.

$$\sum_{co \in CO} C_{co}^{Pro} = \frac{\sum_{co \in CO} C_{co}^{Pro} A_p \gamma [\Delta P - \Delta \pi_{ro}]}{K_C} \quad (3.43)$$

Permeate Flowrate

The permeate flowrate, described by Saif, et al. (2008) is related to the pressure drop across the membrane, the osmotic pressure on the reject side and the number of modules present in the RON according to constraint (3.44). The parameter S_m is the membrane area per module.

$$Q^{Pro} = N_m S_m A_p \gamma [\Delta P - \Delta \pi_{ro}] \quad (3.44)$$

Constraint (44) is then reformulated based on the average solute concentration on the feed side to cater for the number of RO modules in the RON to give constraint (3.45).

$$N_m = \frac{Q^{Pro}}{A_p S_m \gamma [\Delta P - OS \sum_{co \in CO} C_{co}^{Pro}]} \quad (3.45)$$

The cost function of the RON, as represented by constraint (3.46), comprises of variables and physical parameters of the reverse osmosis membrane unit. It consists of the annualised fixed capital cost of turbine, pump, membrane modules as well as the operating costs for pump and pretreatment of chemicals. The operating revenue through energy recovery by the turbine at the retentate side is also incorporated to supplement the cost of energy usage.

$$\begin{aligned}
TAC_r = & K_{mod} N_m + K_{pump} (Pow_{(pump)})^{0.65} + K_{turb} (Pow_{(turb)})^{0.43} \\
& + \frac{Pow_{(pump)} K_{elec} AOT}{\eta_{pump}} + Q^{Fro} K_{chemicals} AOT \\
& - Pow_{(turb)} \eta_{turb} K_{chemicals} AOT
\end{aligned} \tag{3.46}$$

3.6 Performance of Regeneration Units

The performance of a membrane regeneration unit is typically described by the removal ratio and liquid recovery. The removal ratio refers to the fraction of mass load from the feed stream of the regeneration unit that exits the reject stream. This is represented by constraints (3.47) and (3.48) for the ED and RO units respectively.

$$RR_{ed} = \frac{Q^{Red} C_{co}^{Red}}{Q^{Fed} C_{co}^{Fed}} \quad \forall co \in CO \tag{3.47}$$

$$RR_{ro} = \frac{Q^{Rro} C_{co}^{Rro}}{Q^{Fro} C_{co}^{Fro}} \quad \forall co \in CO \tag{3.48}$$

Most published work designates the removal ratio as parameter (Khor et al., 2012, Tank et al., 2009). This work however sets the removal ratio of the organic contaminant COD for the ED unit to be zero (0). This is done for ease of mathematical modelling and efficient operation of the ED unit. Setting the removal ratio of COD to zero means the contaminant in any stream that feeds into the ED unit will exit as it entered since ED units are not capable of treating organic contaminants, besides the formulation of the ED unit in this work is single contaminant based. The removal ratio for the effluent with ionic contaminant is set as variable and will be determined by the optimization model. Similarly the removal ratio for the RO unit is set as a variable for both contaminants, since the RO unit is capable of treating both contaminants. This also gives the optimisation

model the degree of freedom to select the fraction of contaminant that is optimally feasible to be removed.

The liquid recovery on the other hand represents the fraction of feed flowrate that exits through the permeate stream of the regeneration unit. This is shown by constraint (3.49) and (3.50) respectively for both the ED and RO units respectively.

$$LR_{ed} = \frac{Q^{Ped}}{Q^{Fed}} \quad (3.49)$$

$$LR_{ro} = \frac{Q^{Pro}}{Q^{Fro}} \quad (3.50)$$

3.7 Model Constraints

Bounds are set on the flowrates which are used with the binary variables to force constraints to be active or inactive. This is done to reject flowrates that are uneconomically small that could add unnecessary costs to the plant. The lower bounds are set at flowrates below which uneconomical inter piping connections are eliminated and the capacity of the pipe determines the upper bound. In order to achieve this, constraint (3.51) is introduced using a list B. Elements of B, are flowrates that defines the respective units within the superstructure.

$$Let \quad B = \{a, ro, ed, ds, dr, de, es, er, ee, fs, fr, fe, gs, gr, ge\} \quad (3.51)$$

Based on (3.51), constraints (3.52) – (3.55) is introduced, which satisfy all possible bounds for minimum or maximum flowrates that can be used to govern the existence of piping interconnections within the water network superstructure. It can also be used to control the structural features of the design.

$$Q_{j,i}^{bL} Y_{j,i}^b \leq Q_{j,i}^b \leq Q_{j,i}^{bU} Y_{j,i}^b \quad \forall b \in B \quad \forall j \in J \quad \forall i \in I \quad (3.52)$$

$$Q_j^{bL} Y_j^b \leq Q_j^b \leq Q_j^{bU} Y_j^b \quad \forall b \in B \quad \forall j \in J \quad (3.53)$$

$$Q_i^{bL} Y_i^b \leq Q_i^b \leq Q_i^{bU} Y_i^b \quad \forall b \in B \quad \forall i \in I \quad (3.54)$$

$$Q^{bL} Y^b \leq Q^b \leq Q^{bU} Y^b \quad \forall b \in B \setminus \{a, ro, ed\} \quad (3.55)$$

3.8 The Objective Function

Constraint (3.57) represents the objective function which minimises the overall annualised cost of the water network. This includes freshwater cost, wastewater treatment cost and annualised regeneration cost, as well as capital and operating costs of piping interconnections. The costs related to piping are accounted for by specifying an approximate length of pipe, the material of construction and linear velocities through the pipes.

The piping cost $X_{j,i}^b$ which is a function of the Manhattan distance between any units represented by constraint (3.56) is introduced to simplify the presentation of the objective function.

$$X_{j,i}^b = D_{j,i}^b \left(\frac{pQ_{j,i}^b}{3600v} + qY_{j,i}^b \right) \quad (3.56)$$

The subscripts j and i represents interconnections between any sources and sinks respectively. Similarly, X_j^b , X_i^b and X^b in constraints (57), are costs for interconnecting connections from source to regenerators, permeate and reject streams of regenerators to sinks and permeate and reject streams into regeneration units. Where $Y_{j,i}^b$, Y_j^b , Y_i^b and Y^b are the binary variables for existence of piping connections respectively.

$$Obj = \min \left(\left(K_{water} FW + K_{waste} WW \right) AOT + TAC_e + TAC_r + \right. \\ \left. AF \left[\sum_{j \in J} \sum_{i \in I} X_{j,i}^a + \sum_{b \in \{ro, ed\}, j \in J} X_j^b \right. \right. \\ \left. \left. \sum_{b \in \{ds, es, fs, gs\}, i \in I} X_i^b + \sum_{b \in B \setminus \{ro, ed, a, ds, es, fs, gs\}} X^b \right] \right) \quad (3.57)$$

A 1-norm Manhattan distance, $D_{j,i}^b$, D_j^b , D_i^b and D^b is considered for all piping interconnections. All pipes are assumed to be of the same material properties and as a result the carbon steel pipes parameters of p and q are adopted for the piping costs. The symbol v , is the stream flow velocity and AF is the annualisation factor adopted from (Chew, et al., 2008) which is used to annualise the piping cost. The resulting mathematical model is an MINLP. The nonlinear terms are due to the presence of bilinear terms in mass balance equations and power terms in the cost functions of regeneration units. The MINLP model was solved using GAMS 24.2 using the general purpose global optimisation solver BARON.

3.9 Nomenclature

<i>Sets</i>		K^{el}	Electric power cost
$J = \{j j = \text{water source}\}$		K^{mb}	Membrane and capital cost
$I = \{i i = \text{water sink}\}$		K^{tr}	Conversion factor
$B = \{b b = \text{flowrates}\}$		A_p	Water permeability coefficient
$CO = \{co co = \text{contaminants}\}$		AOT	Annual operating time
<i>Parameters</i>		ρ	Density of saline water
a^{LCD}	Constant for limiting current density	n	Number of years
b^{LCD}	Constant for limiting current density	α	Volume factor
z	Electrochemical valence	μ	Viscosity of water
F	Faraday constant	RR^e	Removal ratio for ED unit
S_m	Membrane area per module	RR^r	Removal ratio for RO unit

Q_j^x	Flowrate from source j	β	Shadow factor
$C_{j,co}^x$	Contaminant co from source j	ε	Safety factor
Q_i^z	Flowrate of sink i	μ	Water viscosity
	Maximum allowable contaminant concentration into sink i	γ	Design parameter
$C_{i,co}^U$		ζ	Current utilisation
K_{Chem}	Unit cost of pre-treatment of chemicals	Λ	Equivalent conductance
K_{waste}	Unit cost for waste treatment	v	Velocity of fluid in pipes
K_{water}	Unit cost for freshwater	Q^{Red}	Reject flowrate of ED unit
K_{elect}	Unit cost of electricity	Q^{Fro}	Flowrate into the RO unit
K_{mod}	Unit cost of HFRO membrane module	Q^{Pro}	Permeate flowrate of RO unit
K_{pump}	Cost coefficient of pump	Q^{Rro}	Reject flowrate of RO unit
K_{turb}	Cost coefficient of turbine	Q_i^{ds}	Flowrate from permeate stream of ED into sink i
$D_{2M}/K\delta$	Solute flux constant	Q^{de}	Flowrate from permeate stream of ED unit into ED unit
S_c	Solute permeability coefficient	Q^{dr}	Flowrate from permeate stream of ED unit into RO unit
OS	Osmotic pressure	Q_i^{es}	Flowrate from reject stream of ED unit into sink i
P_F	Feed pressure	$D_{j,i}^b$	Manhattan distance from source to sink
P_p	Permeate pressure of RON	D_j^b	Manhattan distance from source to regeneration units
p, q	Parameter for carbon steel piping	D_i^b	Manhattan distance from permeate and reject stream to sinks
η_{turb}	Turbine efficiency for RO unit	D^b	Manhattan distance from permeate and reject streams to ED and RO units
ρ^{AC}	Membrane resistance		
δ	Cell thickness		
w	Width of cell pair		
η	Pumping efficiency for ED unit		
η_{pump}	Pumping efficiency for RO unit		

<i>Continues variable</i>			
FW	Freshwater flowrate	Q^{gr}	Flowrate from reject stream of RO unit into RO unit
WW	Wastewater flowrate	C^c	Concentration of contaminant in the concentrate stream
$Q_{j,i}^a$	Flowrate from source j to sink i	C_s	Concentration on the shell side
Q_j^{ro}	Flowrate from source j to RO unit	C^{er}	Concentration of recycle stream of the ED unit
Q^{ee}	Flowrate from reject stream of ED unit into ED unit	C_{co}^{Ur}	Maximum allowable contaminant into RO unit
Q^{er}	Flowrate from reject stream of ED unit into RO unit	C_{co}^{Ue}	Maximum allowable contaminant into ED unit
Q_i^{fs}	Flowrate from permeate stream of RO unit into sink i	C_{co}^{Fed}	Concentration of contaminant co into ED unit
Q^{fe}	Flowrate from permeate stream of RO unit into ED unit	C_{co}^{Fro}	Concentration of contaminant co into RO unit
Q_j^{ed}	Flowrate from source j to ED unit	C_{co}^{Ped}	Concentration of contaminant co in the permeate stream of ED unit
Q^{Fed}	Flowrate into the ED unit	C_{co}^{Red}	Concentration of contaminant co in the reject stream of ED unit
Q^{Ped}	Permeate flowrate of ED unit	C_{co}^{Pro}	Concentration of contaminant co in the permeate stream of RO unit
Q^{fr}	Flowrate from permeate stream of RO unit into RO unit	C_{co}^{Rro}	Concentration of contaminant co in the reject stream of RO unit
Q^d	Diluate stream flowrate of ED unit	C^{fc}	Feed concentration in the concentrate stream of ED unit
Q^r	Recycle stream flowrate of ED unit	A	Membrane area of ED unit
Q^c	Concentrate stream flowrate of ED unit	ΔP	Pressure drop
Q^m	Mixing flowrate of ED unit	I^{prac}	Practical current density
Q_i^{gs}	Flowrate from reject stream of RO unit into sink i	$Pow_{(pump)}$	Power of pump
Q^{ge}	Flowrate from reject stream of RO unit into ED unit		

U	Voltage across ED unit	N	Number Electrolysis cell pairs
m	Feed split rate		
I	Electric current	<i>Binary Variables</i>	
V	Velocity of stream in ED unit	$y_{j,i}^b = \begin{cases} 1 \leftarrow \text{Existence of piping interconnection between source and sink,} \\ 0 \leftarrow \text{Otherwise} \end{cases}$	
E^{pump}	Pumping energy		
E^{spec}	Specific energy	$y_i^b = \begin{cases} 1 \leftarrow \text{Existence of piping interconnection between source and regeneration units,} \\ 0 \leftarrow \text{Otherwise} \end{cases}$	
Pow	Power through ED unit		
$Pow_{(turb)}$	Power of turbine	$y_i^b = \begin{cases} 1 \leftarrow \text{Existence of piping interconnection between permeate and reject and sinks,} \\ 0 \leftarrow \text{Otherwise} \end{cases}$	
N_{solute}	Solute flux		
N_{water}	Water flux	$y_i^b = \begin{cases} 1 \leftarrow \text{Existence of piping interconnection between permeate and reject into units,} \\ 0 \leftarrow \text{Otherwise} \end{cases}$	
TAC_r	Total annual cost of ED unit		
TAC_e	Total annual cost of RO unit	$y^b = \begin{cases} 1 \leftarrow \text{Existence of piping interconnection between permeate and reject into units,} \\ 0 \leftarrow \text{Otherwise} \end{cases}$	
$\Delta\pi_{ro}$	Osmotic pressure at retentate side of RO unit		
$\Delta\pi_F$	Osmotic pressure on the feed side	$y^b = \begin{cases} 1 \leftarrow \text{Existence of piping interconnection between permeate and reject into units,} \\ 0 \leftarrow \text{Otherwise} \end{cases}$	
<i>Integer Variables</i>			
N_m	Number of reverse osmosis modules		

3.10 Conclusion

In this chapter a systematic technique is used to formulate a robust mathematical optimization model for simultaneous water and energy minimization. The developed model includes detailed models that describe the design and operation of both ED and RO units within a water network superstructure. The developed model would be applied to two illustrative Case studies in Chapter 4 and one industrial case study in Chapter 5 to demonstrate its applicability. The results obtained from this model will show optimal design variables of the ED and RO units, optimal water consumption as well as optimal water network superstructure configuration for minimum cost.

3.11 References

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APPLICATIONS

CHAPTER 4

ILLUSTRATIVE EXAMPLES

4.1 Introduction

This chapter demonstrates the application of the model developed in Chapter 3 through illustrative examples adopted from literature. The model is applied to illustrative examples: one involving only a single contaminant and one involving multiple contaminants. Following each illustrative example, an analysis and discussion of the results obtained from the model is presented. The aim of the chapter is to provide an explicit explanation and procedure for use of the model constraints developed in Chapter 3.

4.2 Illustrative Example Involving Single Contaminant

The developed mathematical model in Chapter 3 is verified and applied to a pulp and paper illustrative example adopted from Chew et al. (2008). The choice of the illustrative example is motivated by the high number of ionic components produced by the pulp and paper industry. Moreover, the pulp and paper industry involves miscible phase networks consisting of aqueous systems in which streams lose their identities through the mixing process. Hence the illustrative example is suitable for the fixed flowrate method adopted in this work.

Figure 4.1 shows a schematic of a typical pulp and paper plant. Wastewater from the pulp and paper industry is mainly produced in the bleaching section of the plant, and consequently, chlorides and chlorates are the main contaminants of concern.

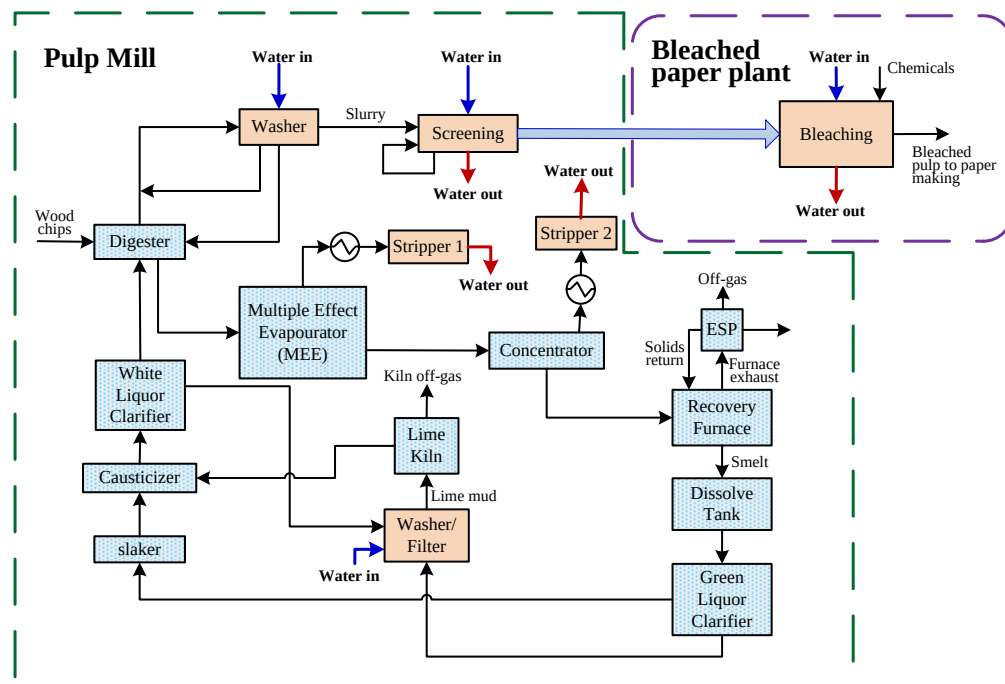


Figure 4.1: Typical pulp and paper plant (Chew et al., 2008)

For ease of understanding and clarity, based on Figure 4.1, Table 4.1 is presented to show the representation of sources and sinks by their respective process units in the pulp and paper plant. It should be noted that sources and sinks 1 to 4 are identified and presented in Table 4.1. The fifth source and sink represents the freshwater source and wastewater sinks respectively which are variable and unknown

Table 4-1: Source sink identification within the pulp and paper plant

Sources	Process unit	Sinks	Process units
1	Stripper 1	1	Washer
2	Screening	2	Screening
3	Stripper 2	3	Washer/filter
4	Bleaching	4	Bleaching
FW	FW	WW	WW

Also worthy of mention is that some process unit's serves as both sources and sinks. Notable among them are screening and bleaching, this are process units that

produces water to satisfy the demands of other units and at the same time consume water.

Table 4.2 contains basic data for the plant water network, including the freshwater source, and the maximum allowable flowrates into five water sinks, including the wastewater sink. There is no limit imposed on the flowrate of freshwater into the process units as well as the flowrate of wastewater to the wastewater sink.

Table 4-2: Basic data for water sources and sinks

Sources, j			Sinks, i		
j	Flowrate (ton/h)	Conc (mg/L)	i	Flowrate (ton/h)	Max. conc (mg/L)
1	2.07	89.4	1	3.26	34.0
2	0.34	272	2	0.34	84.0
3	0.024	18.3	3	1.34	50.0
4	7.22	36.0	4	7.22	6.3
FW	—	0	WW	—	600

Additionally, Table 4.2 details the concentration of contaminant in available water sources and the maximum allowable contaminant concentration into the sinks.

Mass Balances for Sources

Considering the data for the illustrative example in Table 4.2, the sources can be indexed as $j = \{j_1, j_2, j_3, j_4, j_5\}$ and the sinks as $i = \{i_1, i_2, i_3, i_4, i_5\}$. The flowrate from a particular source, as represented by constraint (3.1) in Chapter 3, can be expressed explicitly as the set of constraints (4.1) to (4.5).

$$2.07 = \sum_{i=i_1}^{i_5} Q_{j_1,i}^a + Q_{j_1}^{ro} + Q_{j_1}^{ed} \quad (4.1)$$

$$0.34 = \sum_{i=i_1}^{i_5} Q_{j_2,i}^a + Q_{j_2}^{ro} + Q_{j_2}^{ed} \quad (4.2)$$

$$0.024 = \sum_{i=i_1}^{i_5} Q_{j_3,i}^a + Q_{j_3}^{ro} + Q_{j_3}^{ed} \quad (4.3)$$

$$7.22 = \sum_{i=i_1}^{i_5} Q_{j_4,i}^a + Q_{j_4}^{ro} + Q_{j_4}^{ed} \quad (4.4)$$

$$Q_{j_5}^x = \sum_{i=i_1}^{i_5} Q_{j_5,i}^a + Q_{j_5}^{ro} + Q_{j_5}^{ed} \quad (4.5)$$

Mass and Concentration Balance for Regeneration Units

The mass load into the regeneration units, constraints (3.4) and (3.5) from Chapter 3 is represented by constraints (4.6) and (4.7). Although, the general model formulation is capable of catering for multiple contaminants, the illustrative example in this section concerns only a single contaminant. It should be however noted that density is assumed constant hence the volumetric flowrates are additive. The set of contaminants may be indexed as $co = \{co_1\}$.

$$108 \geq \frac{\sum_{j=j_1}^{j_5} Q_j^{ed} C_{j,co_1}^x + Q^{de} C_{co_1}^{Ped} + Q^{ee} C_{co_1}^{Red} + Q^{fe} C_{co_1}^{Pro} + Q^{ge} C_{co_1}^{Rro}}{Q^{Fed}} \quad (4.6)$$

$$330 \geq \frac{\sum_{j=j_1}^{j_5} Q_j^{ro} C_{j,co_1}^x + Q^{dr} C_{co_1}^{Ped} + Q^{er} C_{co_1}^{Red} + Q^{fr} C_{co_1}^{Pro} + Q^{gr} C_{co_1}^{Rro}}{Q^{Fro}} \quad (4.7)$$

Constraint (3.10) in Chapter 3, which represents the water balance into a particular sink, is represented by constraints (4.8) to (4.12). It is worth noting that the fifth sink, $Q_{i_5}^z$, is the wastewater sink which is a variable and unknown, hence constraint (4.12) is presented without a parameter value.

$$3.26 = \sum_{j=j_1}^{j_5} Q_{j,i_1}^a + Q_{i_1}^{ds} + Q_{i_1}^{es} + Q_{i_1}^{fs} + Q_{i_1}^{gs} \quad (4.8)$$

$$0.34 = \sum_{j=j_1}^{j_5} Q_{j,i_2}^a + Q_{i_2}^{ds} + Q_{i_2}^{es} + Q_{i_2}^{fs} + Q_{i_2}^{gs} \quad (4.9)$$

$$1.34 = \sum_{j=j_1}^{j_5} Q_{j,i_3}^a + Q_{i_3}^{ds} + Q_{i_3}^{es} + Q_{i_3}^{fs} + Q_{i_3}^{gs} \quad (4.10)$$

$$7.22 = \sum_{j=j_1}^{j_5} Q_{j,i_4}^a + Q_{i_4}^{ds} + Q_{i_4}^{es} + Q_{i_4}^{fs} + Q_{i_4}^{gs} \quad (4.11)$$

$$Q_{i_5}^z = \sum_{j=j_1}^{j_5} Q_{j,i_5}^a + Q_{i_5}^{ds} + Q_{i_5}^{es} + Q_{i_5}^{fs} + Q_{i_5}^{gs} \quad (4.12)$$

Similarly, constraints (4.13) to (4.15) express the mass load into the respective sinks.

$$34.0 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_1}^a C_{j,co_1}^x + Q_{i_1}^{ds} C_{co_1}^{Ped} + Q_{i_1}^{es} C_{co_1}^{Red} + Q_{i_1}^{fs} C_{co_1}^{Pro} + Q_{i_1}^{gs} C_{co_1}^{Rro}}{Q_{i_1}^z} \quad (4.13)$$

$$84.0 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_2}^a C_{j,co_1}^x + Q_{i_2}^{ds} C_{co_1}^{Ped} + Q_{i_2}^{es} C_{co_1}^{Red} + Q_{i_2}^{fs} C_{co_1}^{Pro} + Q_{i_2}^{gs} C_{co_1}^{Rro}}{Q_{i_2}^z} \quad (4.14)$$

$$50.0 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_3}^a C_{j,co_1}^x + Q_{i_3}^{ds} C_{co_1}^{Ped} + Q_{i_3}^{es} C_{co_1}^{Red} + Q_{i_3}^{fs} C_{co_1}^{Pro} + Q_{i_3}^{gs} C_{co_1}^{Rro}}{Q_{i_3}^z} \quad (4.14)$$

$$6.3 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_4}^a C_{j,co_1}^x + Q_{i_4}^{ds} C_{co_1}^{Ped} + Q_{i_4}^{es} C_{co_1}^{Red} + Q_{i_4}^{fs} C_{co_1}^{Pro} + Q_{i_4}^{gs} C_{co_1}^{Rro}}{Q_{i_4}^z} \quad (4.14)$$

$$600 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_5}^a C_{j,co_1}^x + Q_{i_5}^{ds} C_{co_1}^{Ped} + Q_{i_5}^{es} C_{co_1}^{Red} + Q_{i_5}^{fs} C_{co_1}^{Pro} + Q_{i_5}^{gs} C_{co_1}^{Rro}}{Q_{i_5}^z} \quad (4.15)$$

4.2.1 Process Data for Regeneration Units

Based on the illustrative example adopted for this work, the operational parameters for the regeneration units are as per Tsiakis & Papageorgiou, (2005) for the ED unit and Khor et al. (2011) for the RO unit. Tables 4.3 and 4.4 contain process data for ED and RO units, whereas Table 4.5 contains economic data for the detailed design of both regeneration units. These parameters serve as bounds

to facilitate the convergence of the model. Table 4.6 contains data for the Manhattan distances between units.

Electrodialysis Unit

This section entails the representation of the detailed design equations of the electrodialysis membrane regeneration unit as presented in Chapter 3. The parameter values in Tables 4.2 and 4.4 are substituted into the constraints of the ED design model. For simplicity and ease of understanding, equations (3.12) to (3.33) are explicitly presented with the parameter symbols replaced by actual values as follows:

Table 4-3: Input data parameters into the ED unit.

Parameter	Value
Current utilization, ζ	0.9
Cell width, w	0.42 m
Equivalent conductance, Λ	10.5 m ² /keq
Faraday's constant, F	9.65x10 ⁷ As/keq
Electrochemical valence, z	1
Constant for limiting current density, a^{LCD}	25000
Constant for limiting current density, b^{LCD}	0.5
Membrane resistance, ρ^{AC}	0.0007 Ω m ²
Volume factor, α	0.8
Velocity in pipes, v	1 m/s
Shadow factor, β	0.7
Maximum equipment life, t^{max}	5 years
Safety factor, ε	0.7
Pump efficiency, η	0.7
Liquid recovery, LR^e	0.7
Conversion factor, K^{tr}	27.2
Electric power costs, K^{el}	0.12 \$/kWh
Membrane and capital costs, K^{mb}	150 \$/m ²

Table 4-4: Input data parameters into the RO unit

Parameter	Value
Shell side pressure drop, ΔP_{shell}	0.4 atm
Osmotic pressure coefficient, OS	4.083×10^{-4} atm
Solute permeability coefficient, S_C	1.82×10^{-8} m/s
Water viscosity, μ	9.84×10^{-4} kg/(m.s)
Water permeability coefficient, A_P	5.573×10^{-8} m/(s.atm)
Permeate pressure, P_p	1 atm
Atmospheric pressure, P_{atm}	1 atm
Design parameter, γ	0.694
Pump efficiency, η_{pump}	0.7
Turbine efficiency, η_{turb}	0.7
Membrane area per module, S_m	180 m ²
Liquid recovery, LR^r	0.7
Cost coefficient for pump, K^{pump}	6.5 \$(year.W ^{0.65})
Cost coefficient for turbine, K^{turb}	18.4 \$(year.W ^{0.43})
Unit cost of HFRO membrane module K^{mod}	2300 \$/year

Table 4-5: Economic data for case study

Parameter	Value
Annual operating time, AOT	8760 h
Cost of electricity, K^{el}	0.12 \$/kWh
Unit cost of pretreatment of chemicals, K^{chem}	3×10^{-5} \$/kg
Annualization factor, AF	0.23
Unit cost of freshwater, K^{FW}	0.001 \$/kg
Unit cost of effluent treatment, K^{WW}	0.001 \$/kg
Parameter for carbon steel piping, p	7200
Parameter for carbon steel piping, q	2500

Electric Current

In the electric current equation (3.12) in Chapter 3, the Faraday constant, electrochemical valence as well as the current utilization constant, are parameters which are explicitly represented in constraint (4.16).

$$I = \frac{Q^d (C_{co_1}^{Fed} - C_{co_1}^{Ped}) 9.65 \times 10^7 \times 1}{0.9N} \quad (4.16)$$

The concentration difference and the practical limiting current density constraints (3.13) and (3.14) in Chapter 3, are presented by equations (4.17) and (4.18) respectively. As can be seen in constraint (4.18), the practical limiting current density consists of a safety factor and constants for limiting current density, all of which are parameters.

$$C_{co_1}^{\Delta} = C_{co_1}^{Fed} - C_{co_1}^{Ped} = C_{co_1}^C - C_{co_1}^{fc} \quad (4.17)$$

$$I^{Prac} = 0.7 \times 2500 \times C_{co_1}^d (U)^{0.5} \quad (4.18)$$

Stack Design Considerations

The membrane area constraint (3.16) in Chapter 3, is explicitly presented with the corresponding parameter values in Constraint (4.19). The parameter values are the equivalent electrical conductivity, Λ , the area resistance of anion and cation exchange membranes, ρ^{AC} , the cell thickness, δ , the current utilization, ζ , the electrochemical valence, z , the Faraday constant, F , as well as a correction factor, β .

$$A = \frac{\left[\ln \frac{C_{co_1}^C C_{co_1}^{Fed}}{C_{co_1}^{Ped} C_{co_1}^{fc}} + \frac{10.5 \times 0.0007 (C_{co_1}^{Fed} - C_{co_1}^{Ped})}{0.00065} \right] C_{co_1}^{Ped} Q^d 9.65 \times 10^5 \times 1}{\left[\frac{C_{co_1}^{Ped}}{C_{co_1}^{Ped}} + 1 + \frac{10.5 C_{co_1}^d}{0.00065} 0.0007 \right] I^{Prac} 0.9 \times 0.7} \quad (4.19)$$

Energy Considerations

Constraint (3.17) in Chapter 3 which represents the energy required for the operation of an ED regeneration unit is presented with the parameter values in constraints (4.20).

$$U = \frac{(C_{co_1}^{Fed} - C_{co_1}^{Ped})NQ^d 9.65 \times 10^5 \times 1}{0.9A} \left[\frac{0.00065 \ln \frac{C_{co_1}^C C_{co_1}^{Fed}}{C_{co_1}^{Ped} C_{co_1}^{fc}}}{10.5(C_{co_1}^{Fed} - C_{co_1}^{Ped})} + 0.0007 \right] \quad (4.20)$$

Constraint (4.21) represents the liquid recovery constraint with the corresponding parameter value.

$$0.95 = \frac{Q^{Ped}}{Q^d} \quad (4.21)$$

Similarly, the permeate flowrate constraint (3.15) pressure drop constraint (3.20), pumping energy constraint (3.21), and the material balance constraints (3.22) to (3.30) around the ED regeneration unit can be expressed with their parameter values as is shown in constraints (4.16) to (4.21).

The Total Annualised Cost of the ED regeneration unit is represented by constraint (4.22), which is comprised of the parameter values as well as the variables. The cost of membrane material, the annual operating time, the number of years of operation and the electrical energy cost are all parameters in the equation which are included in constraint (4.22) for ease of explanation.

$$TAC_e = \frac{150}{5} + 8760 \times 0.12 Q^{Ped} [E^{Pump} + E^{Spec}] \quad (4.22)$$

Hollow Fibre Reverse Osmosis Unit

This section entails the presentation of expansive, explicit equations of the RO membrane regeneration unit as developed in Chapter 3. Tables 4.3 and 4.4 contain the input data parameters and the economic data for the case studies. Parameter values are substituted into the detailed design equations for purposes of clarity and meaning as well as ease of comprehension.

Membrane Transport Equations

Constraints (3.34) and (3.35), which represent the solute and water flux constraints in Chapter 3, are represented with their parameter values in constraints (4.23) and (4.24) respectively.

$$N_{Solute} = [1.82 \times 10^{-8}] C_S \quad (4.23)$$

$$N_{Water} = 5.573 \times 10^{-8} \left[\Delta P - \frac{\pi_F}{C_{CO_1}^{Fro}} C_S \right] 0.694 \quad (4.24)$$

Transmembrane Pressure

Constraints (3.37) and (3.39), which represent the transmembrane pressure across the RO regeneration membrane unit, are transformed with their parameter values in constraints (4.25) and (4.26).

$$\Delta P = \frac{(P_F + P_R)}{2} - 1 \quad (4.25)$$

$$P_F = \Delta P + \left[\frac{0.4}{2} + 1 \right] \quad (4.26)$$

Average Concentration on the feed Side

Constraints (3.42) concerning the osmotic pressure on the retentate side and (3.43) for the osmotic pressure on the feed side are presented in constraints (4.27) and (4.28) respectively. The area permeability constant AP , the osmotic pressure coefficient OS , the solute permeability coefficient K_C , as well as the design

constant γ , are all parameters which have been substituted with their respective values.

$$\Delta\pi_{ro} = 4.083 \times 10^{-4} \sum_{co=c_{o1}}^{c_{o1}} C_{c_{o1}}^{Fro} \quad (4.27)$$

$$\sum_{co=c_{o1}}^{c_{o1}} C_{c_{o1}}^{Fro} = \frac{\sum_{co=c_{o1}}^{c_{o1}} C_{c_{o1}}^{Pro} 5.73 \times 10^{-8} \times 0.694 [\Delta P - \Delta\pi_{ro}]}{1.82 \times 10^{-8}} \quad (4.28)$$

Permeate Flowrate and Number RO Modules

Constraints (4.29) and (4.30) represent the permeate flowrate based on the osmotic pressure and the number of RO modules. The membrane area per module, S_m , the area permeability constant AP , design constant γ , as well as the osmotic pressure coefficient OS are all parameters which are duly represented in these constraints.

$$Q^{Pro} = 180 \times 5.573 \times 10^{-8} \times 0.694 N_m [\Delta P - \Delta\pi_{ro}] \quad (4.29)$$

$$N_m = \frac{Q^{Pro}}{5.573 \times 10^{-8} \times 0.694 \left[\Delta P - 4.083 \times 10^{-4} \sum_{co=c_{o1}}^{c_{o1}} C_{c_{o1}}^{Fro} \right]} \quad (4.30)$$

Annualised Cost of the RO Regeneration Unit

The Total Annualised Cost of the RO membrane regeneration unit is expressed with the appropriate parameter values in constraint (4.31). The parameters include the cost of RO membrane modules, the cost of pumping, the cost of the turbine, the cost of electricity, the annual operating time, the pump and turbine efficiency and the cost of pre-treatment chemicals.

$$\begin{aligned}
TAC_r = & 2300N_m + 6.5(POW_{(pump)})^{0.65} + 18.4(POW_{(turb)})^{0.43} \\
& + \frac{0.12 \times 8760 POW_{(pump)}}{0.7} + 3 \times 10^{-5} \times 8760 Q^{Fro} \\
& - 0.7 \times 3 \times 10^{-5} \times 8760 POW_{(turb)}
\end{aligned} \tag{4.31}$$

Model Constraints

Based on Chapter 3, under the Model Constraints section, the set $B = \{a, ro, ed, ds, dr, de, es, er, ee, fs, fr, fe, gs, gr, ge\}$ is introduced, where B represents the respective flowrates across the units within the superstructure. Specific bounds are imposed in order to govern the minimum and maximum allowable flowrate within the piping interconnections. Constraints (4.32) to (4.36) represent the specific bounds on the flowrates for all possible piping interconnection between sources $j = \{j_1, j_2, j_3, j_4, j_5\}$ and sinks $i = \{i_1, i_2, i_3, i_4, i_5\}$.

$$1 \times 10^{-4} Y_{j_1, i_1}^a \leq Q_{j_1, i_1}^a \leq Y_{j_1, i_1}^a \quad 20 \tag{4.32}$$

$$1 \times 10^{-4} Y_{j_1, i_2}^a \leq Q_{j_1, i_2}^a \leq Y_{j_1, i_2}^a \quad 20 \tag{4.33}$$

$$1 \times 10^{-4} Y_{j_1, i_3}^a \leq Q_{j_1, i_3}^a \leq Y_{j_1, i_3}^a \quad 20 \tag{4.34}$$

$$1 \times 10^{-4} Y_{j_1, i_4}^a \leq Q_{j_1, i_4}^a \leq Y_{j_1, i_4}^a \quad 20 \tag{4.35}$$

$$1 \times 10^{-4} Y_{j_1, i_5}^a \leq Q_{j_1, i_5}^a \leq Y_{j_1, i_5}^a \quad 20 \tag{4.36}$$

Similarly, the flowrates for the piping interconnections from sources j_2, j_3, j_4, j_5 and sinks i_2, i_3, i_4, i_5 to regenerator units, permeate and reject streams, and the reuse and recycle streams can be illustrated in the same fashion as is shown in constraints (4.32) to (4.36).

Piping Costs

The piping costs, which are functions of the distance between relevant units, the material of construction and the linear velocities through the pipes, are expressed in this section. Constraints (4.37) to (4.41) express the costs of piping between source j_1 , and sinks, i_1 , i_2 , i_3 , i_4 , and i_5 . Table 4.5 shows the data for Manhattan distances between different units. Specifically, it contains data for the distances between the sources and sinks, sources and regenerator units, regenerator permeate streams and sinks as well as reject streams and sinks. It is however, worth noting that the distances for the reuse and recycle streams of the regenerator permeate and reject streams into the regenerator units are the same.

Table 4-6: Data for the Manhattan Distance (m) for the Case Studies

	Sinks					Regenerator units	
Sources	1	2	3	4	5	ED	RO
1	50	50	50	60	80	50	50
2	60	50	60	70	90	40	40
3	50	50	50	60	80	65	50
4	60	50	60	70	90	100	50
5	50	50	50	60	80	40	50
Reg. units							
ED	80	70	60	70	60		
RO	60	50	60	70	80		

$$X_{j_1, i_1}^a = (50)_{j_1, i_1}^a \left(\frac{7200Q_{j_1, i_1}^a}{3600 \times 1} + 2500Y_{j_1, i_1}^a \right) \quad (4.37)$$

$$X_{j_1, i_2}^a = (50)_{j_1, i_2}^a \left(\frac{7200Q_{j_1, i_2}^a}{3600 \times 1} + 2500Y_{j_1, i_2}^a \right) \quad (4.38)$$

$$X_{j_1, i_3}^a = (50)_{j_1, i_3}^a \left(\frac{7200Q_{j_1, i_3}^a}{3600 \times 1} + 2500Y_{j_1, i_3}^a \right) \quad (4.39)$$

$$X_{j_1, i_4}^a = (60)_{j_1, i_4}^a \left(\frac{7200Q_{j_1, i_4}^a}{3600 \times 1} + 2500Y_{j_1, i_4}^a \right) \quad (4.40)$$

$$X_{j_1, i_5}^a = (80)_{j_1, i_5}^a \left(\frac{7200Q_{j_1, i_5}^a}{3600 \times 1} + 2500Y_{j_1, i_5}^a \right) \quad (4.41)$$

Similarly, the costs of piping from sources j_2, j_3, j_4, j_5 to sinks i_2, i_3, i_4, i_5 , , regenerator units to sinks, permeate and reject streams to sinks, as well as reuse and recycle streams can be modelled in a similar fashion to constraints (4.37) to (4.41).

Objective Function

The objective function, which is comprised of the overall annualised cost of the water network superstructure, is expressed with the parameter values as shown in constraint (4.42).

$$Obj = \min \left\{ \begin{aligned} & (0.001FW + 0.001WW)8760 + TAC_e + TAC_r + \\ & 0.23 \left[\sum_{j=j_1}^{j_5} \sum_{i=i_5}^{i_5} X_{j,i}^a + \sum_{j=j_1}^{j_5} X_j^{ro} X_j^{ed} + \sum_{i=i_1}^{i_5} X_i^{ds} X_i^{es} X_i^{fs} X_i^{gs} \right. \\ & \left. + \sum X^{dr} X^{de} X^{er} X^{ee} X^{fr} X^{fe} X^{gr} X^{ge} \right] \end{aligned} \right\} \quad (4.141)$$

4.3 Results and Discussion for Single Contaminant Illustrative Example

This section entails the presentation and discussion of the results obtained through the application of the proposed model to the single contaminant illustrative example. The illustrative example was applied to three different scenarios in order to ascertain the benefits of considering a comprehensive network of membrane regeneration units within the overall water network. Hence, a detailed analysis and comparison of the results will be outlined based on the three scenarios considered.

4.3.1 Scenarios Considered

- (i) Scenario 1 considers a model of the water network without regeneration. As such, the detailed design constraints as well as mass balance constraints describing the membrane partitioning regenerator units are eliminated. The resultant model is a mixed integer linear program (MILP), which requires less computational time to solve.
- (ii) Scenario 2 considers a water network with regeneration units based on a “black-box” approach. This formulation approach results in a mixed integer nonlinear program (MINLP) as a result of the presence of bilinear terms in the regenerator balance equations. Detailed design constraints of both ED and RO membrane regenerators are omitted in the formulation. The cost of regeneration is characterised by linear cost functions based on the flow through the regeneration unit. The “black-box” formulation also considers both a fixed and a variable removal ratio in order to describe the performance of the regeneration units.
- (iii) Scenario 3 considers detailed models of both ED and RO regeneration units incorporated into the overall water network, objective function and synthesis, in order to obtain more accurate optimal operating values, costs and design parameters. The formulation for scenario 3 is characterised as a mixed integer nonlinear program (MINLP). This is a result of the ED and RO models being highly nonlinear, as they involve logarithmic, bilinear and exponential terms as

well as the decision variables (0, 1) required in selecting the piping interconnections between units.

The formulation also considers a fixed and variable removal ratio setting for ED and RO membrane regeneration units

For scenarios 2 and 3, the optimisation was conducted for both fixed and variable removal ratios. For comparison, in both cases the fixed removal ratio was set at a value of 0.7 for both ED and RO membrane regeneration units. The results of scenarios 1, 2, and 3 were compared in order to analyse the trade-offs between water consumption, wastewater generation, regeneration cost, as well as overall water network cost present in each case.

4.3.2 Results

The optimal results for all scenarios are presented in Table 4.7. The results considered the amount of freshwater consumed, wastewater generated, total water network cost as well as the computational time for all scenarios considered.

Table 4-7: Optimal results of water network based on the case study

	Scenario 1	Scenario 2		Scenario 3	
		Fixed RR	Variable RR	Fixed RR	Variable RR
Freshwater use (t/h)	18.300	11.145	10.012	11.183	10.189
% of freshwater savings		39.1	45.3	38.89	44.32
Wastewater generated (t/h)	15.785	8.958	7.796	8.996	7.742
% of wastewater saved		43.2	50.6	43.01	50.95
Total cost (million \$)	1.170	0.597	0.508	0.626	0.566
CPU time (s)	0.06	865	2764.20	687.50	16709.78

Scenario 1, which is the base case scenario, consumed up to 18.300 t/h freshwater and produced 15.785 t/h wastewater. The total cost of the water network for this scenario is \$1.17 M. The computational time was less than a second, which is attributed to the linearity and reduced size of the model. The optimal water

network configuration and flowsheet are presented in Figures 4.2 and 4.3, respectively. The results obtained by scenario 1 serve as a basis for comparison between scenarios 2 and 3.

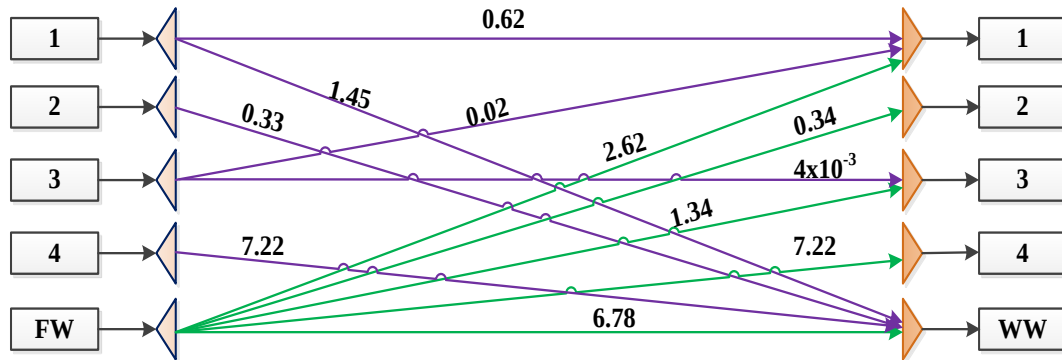


Figure 4.2: Optimum water network configuration for scenario 1 (direct water usage)

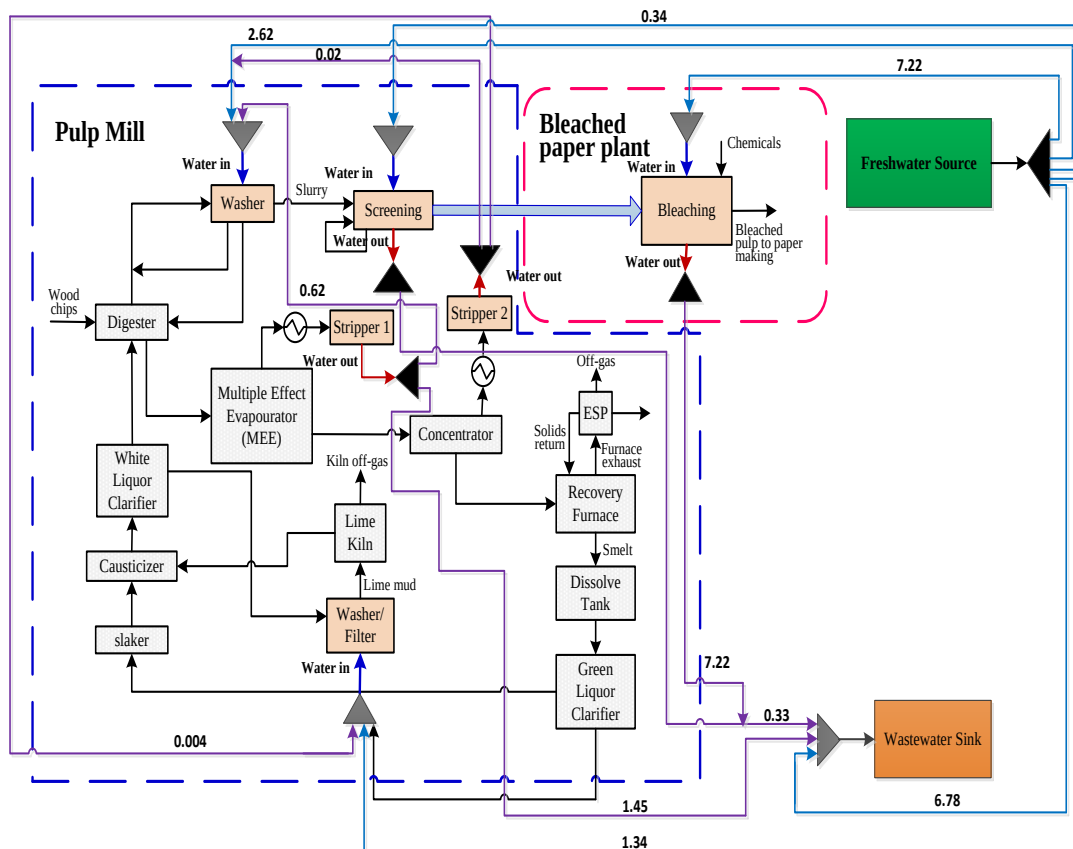


Figure 4.3: Optimum flowsheet for scenario 1 (direct water usage)

The results for scenario 2, including both fixed and variable removal ratios are presented in Table 4.7. The fixed removal ratio formulation indicated an optimal freshwater consumption requirement of 11.145 t/h with 8.958 t/h of wastewater generation. This results in a 39.1% reduction in freshwater consumption and a 43.2% reduction in wastewater generation when compared to the base case in scenario 1. Figures 4.4 and 4.5 display the optimal water network configuration and flowsheet for the fixed removal ratio case under scenario 2. The total cost of the water network is \$0.597 M. The computational time required for the solution was 865 seconds.

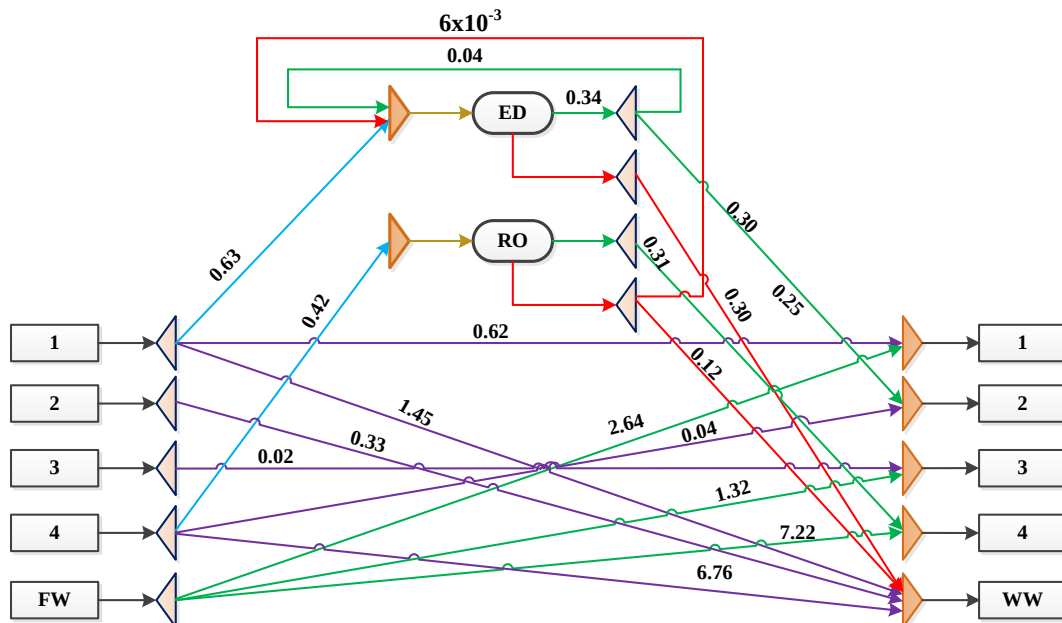


Figure 4.4 Optimum water network configuration for scenario 2 (fixed removal ratio)

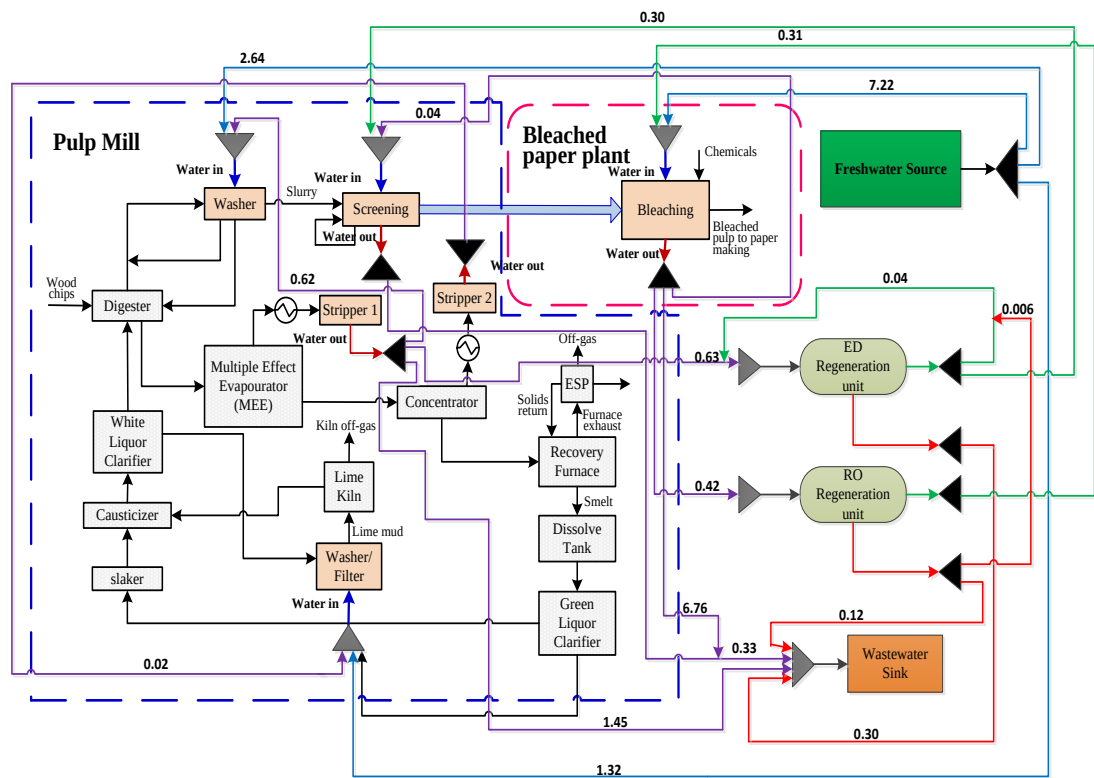


Figure 4.5: Optimum flowsheet for scenario 2 (fixed removal ratio)

The variable removal case under scenario 2 required 10.012 t/h of freshwater and produced 7.796 t/h of wastewater. This translates to a 45.3% reduction in freshwater consumption and 50.6% reduction in wastewater generation when compared to scenario 1. The optimal water network configuration and flowsheet for the variable removal ratio formulation, under scenario 2, is represented by Figures 4.6 and 4.7, respectively. The total cost of the water network is \$0.508 M whereas the computational time required for model solution was 2764.20 seconds.

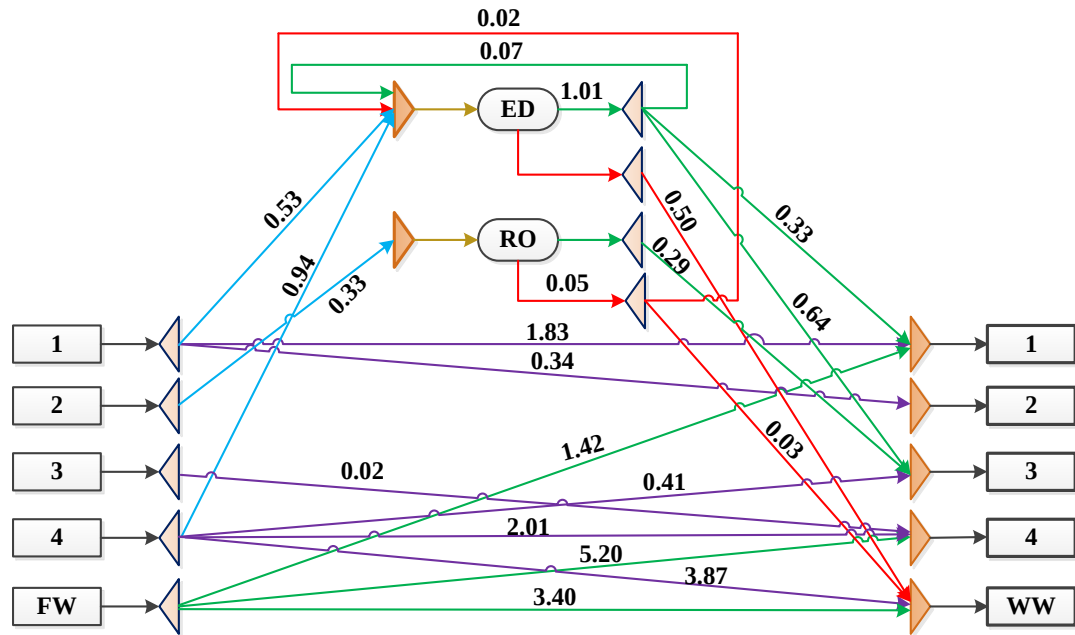


Figure 4.6: Optimum water network configurations for scenario 2 (variable removal ratio)

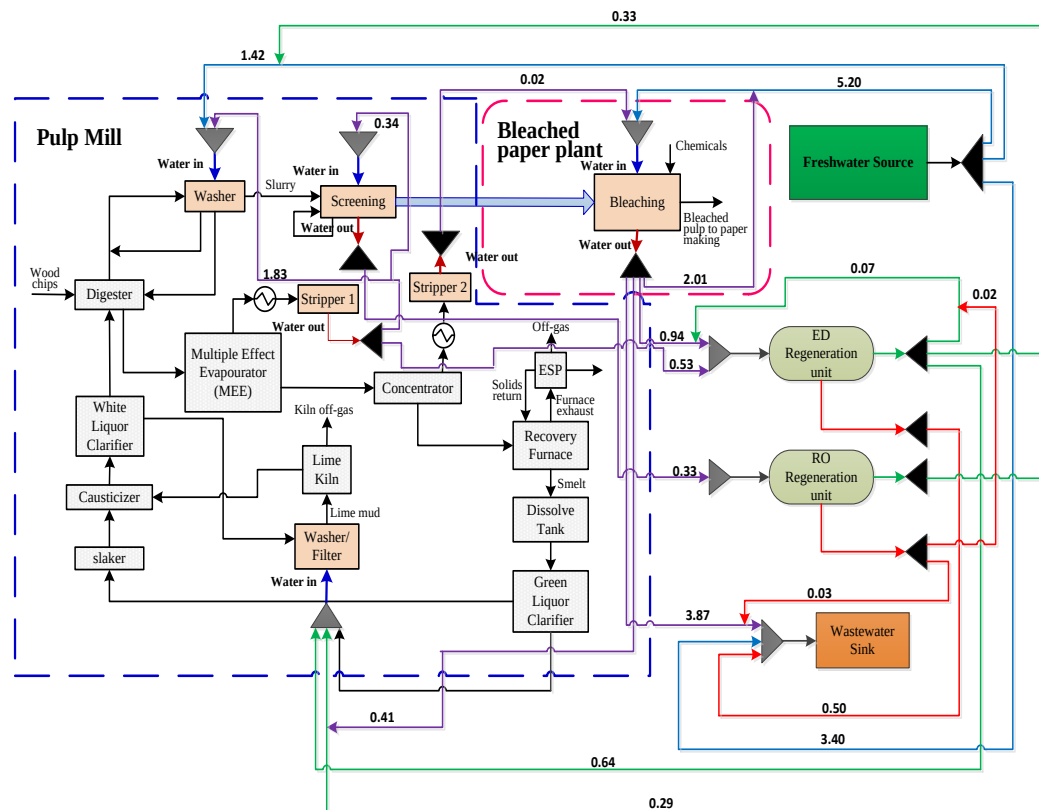


Figure 4.7: Optimum flowsheet for scenario 2 (variable removal ratio)

The results for scenario 3 illustrated in Table 4.7 includes both the fixed and variable removal ratio formulations. The fixed removal ratio formulation indicated a requirement of 11.183 t/h freshwater and a wastewater production rate of 8.996 t/h. This results in a 38.89% reduction in freshwater consumption and a 43.02% reduction in wastewater generation as compared to scenario 1. The total water network cost is \$0.626 M and the computational time required was 687.50 seconds. Figures 4.8 and 4.9 show the optimal water network configuration and flowsheet for the fixed variable case under scenario 3.

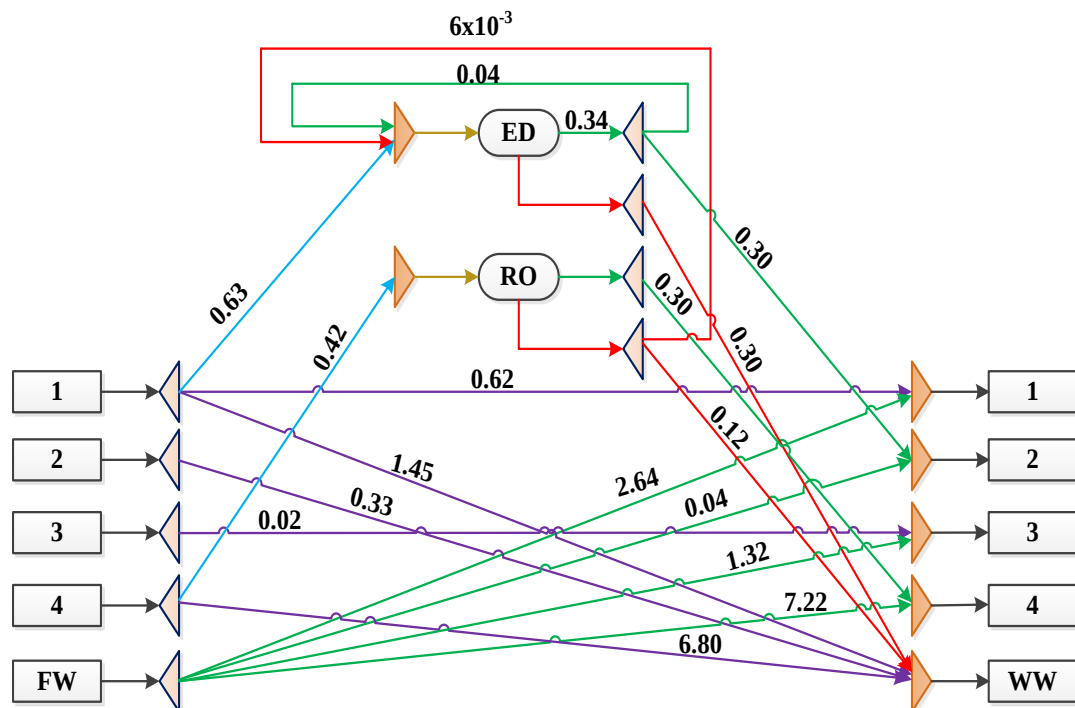


Figure 4.8: Optimum water network configuration for scenario 3 (fixed removal ratio)

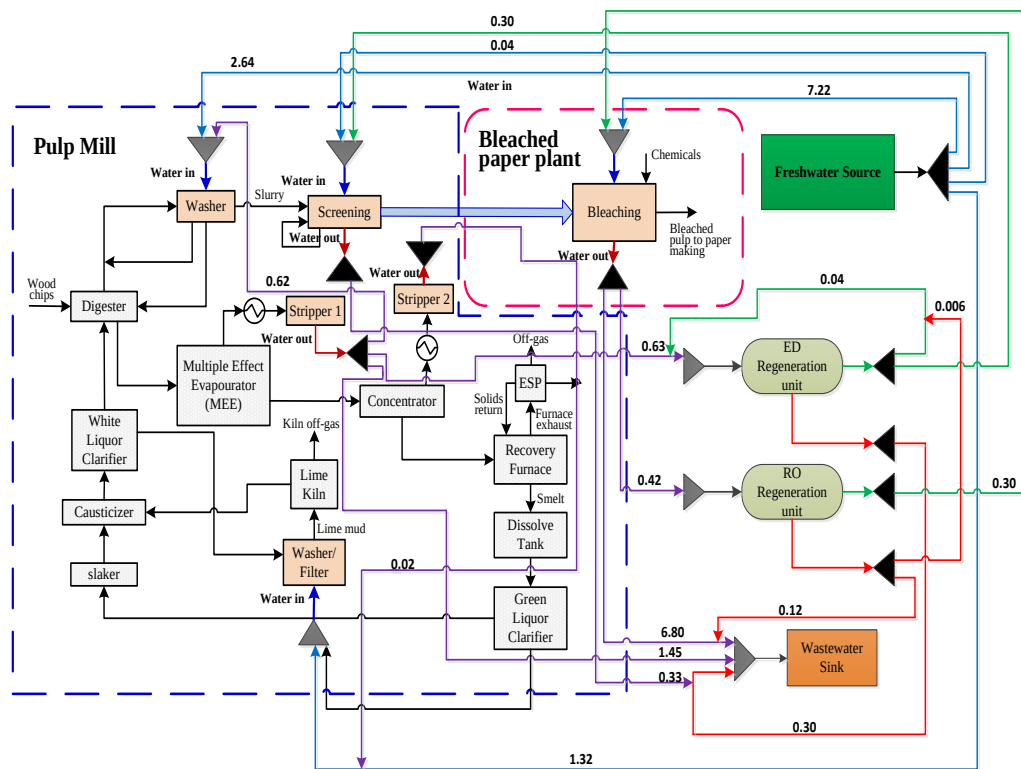


Figure 4.9: Optimum flowsheet for scenario 3 (fixed removal ratio)

The variable removal ratio formulation under scenario 3, on the other hand, indicated a requirement of 10.189 t/h freshwater and a wastewater production rate of 7.742 t/h. This results in a 44.32% reduction in freshwater use and a 50.95% reduction in wastewater generation as compared to scenario 1. The total water network cost is \$0.566 M and the computational time required for solution was 16709.79 seconds. Figures 4.10 and 4.11, respectively show the optimal design configurations and flowsheets for the variable removal ratio formulations under scenario 3.

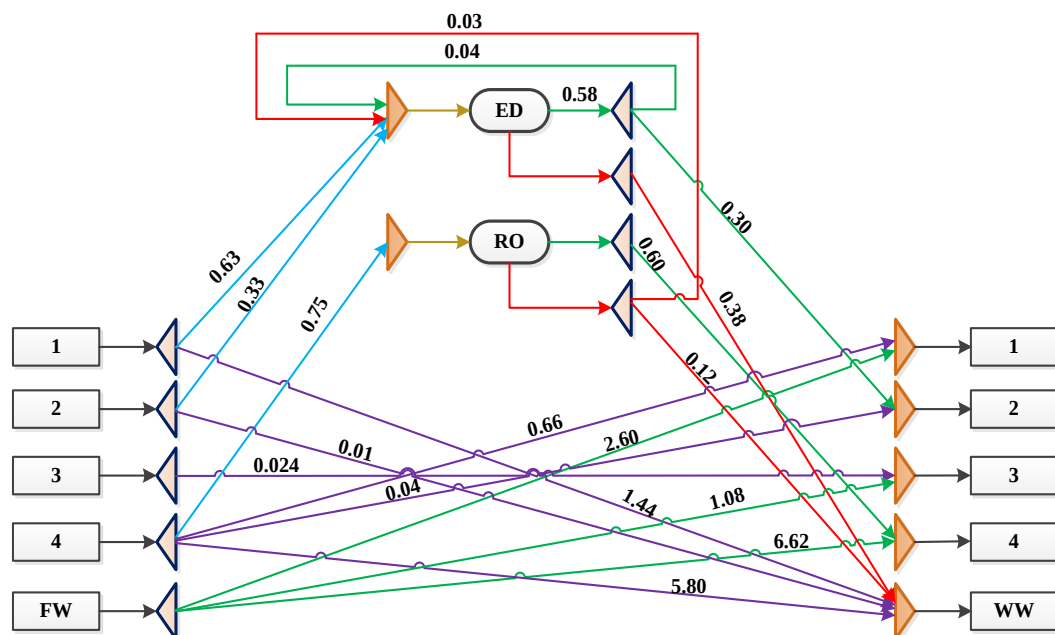


Figure 4.10: Optimum water network configuration for scenario 3 (fixed removal ratio)

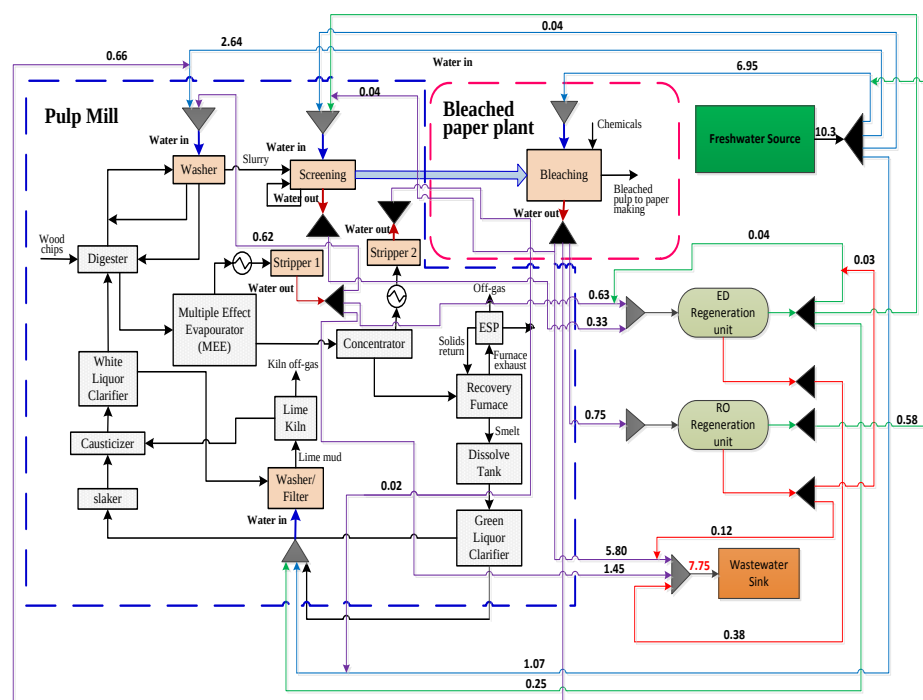


Figure 4.11: Optimum flowsheet for scenario 3 (variable removal ratio)

Scenarios 2 and 3 both presented solutions with a reduction in freshwater consumption, wastewater generation as well as the total annualised water network

cost as compared to the scenario without wastewater regeneration. However, scenario 3 provided the best optimum solution as it incorporated the detailed models of the regeneration units. The results of scenario 3 are displayed in Figures 4.8, 4.9, 4.10 and 4.11. Figures 4.2 and 4.3, display the optimal configuration and flowsheet of scenario 1, whereas Figures 4.4, 4.5, 4.6 and Figure 4.7 represent the results for scenario 2. Scenario 3 resulted in a significant reduction in water network cost as well as freshwater consumption and wastewater generation as compared to the direct water network model without regeneration. However, there was an increase in the total water network cost when compared to scenario 2. This is as a result of scenario 3 being a more accurate representation of the total water network as it incorporates a detailed design of the membrane regeneration units. The cost function in scenario 3 presents accurate expression of the regeneration cost as compared to the linear cost function used in scenario 2. Apart from representing accurate costs of water regeneration units, the detailed model presented in this work is also capable of determining optimal design configurations of the membrane regeneration units for minimum energy usage.

4.3.3 Comparative Analysis

The analysis and comparison of all the scenarios considered showed that scenarios 2 and 3 are both better options than scenario 1. This is as a result of the high freshwater consumption and wastewater generation in scenario 1 as compared to scenarios 2 and 3. Additionally, the cost of the water network in scenario 1 was comparatively higher than scenarios 2 and 3. The higher water network cost is as a result of high freshwater consumption and wastewater generation. The insights drawn from the results indicate that there is merit in incorporating regeneration separation units within water network synthesis for the partial treatment of wastewater and its subsequent reuse and recycle.

Having ascertained that integrating membrane partitioning regeneration units within water network synthesis and optimization is an important technique for the sustainable use of water, focus should be directed towards scenarios 2 and 3. Analysis of the results within scenario 2, between the fixed removal ratio and variable removal ratio formulations, indicates that the variable removal ratio

formulation yields better objective values. The variable removal ratio formulation results in reduced freshwater consumption and wastewater generation as compared to the fixed removal ratio formulation.

The computational time required for the solution of the variable removal ratio formulation is, however, higher than that for the formulation concerning a fixed removal ratio. Similarly, the variable removal ratio formulation under scenario 3 presented better results in terms of freshwater consumption, wastewater generation and total water network cost. The computational time required for the variable removal ratio formulation is also higher than the fixed removal ratio in scenario 3.

The specification of the removal ratios in scenarios 2 and 3, results in a more constrained feasible region. The consequence is a reduced search space for the solution procedure and hence a lower computational time is required for the solution. Setting the removal ratio as a variable increases the number of variables in the overall model. It also increases the size of the feasible region as the model introduces an additional degree of freedom in the search for optimal design parameters.

4.3.4 Discussion

By considering the results in Table 4.7, it is evident that a variable removal ratio in scenario 3 presents the optimal configuration, since the model is allowed to choose the performance parameters of the membrane regenerators. The results also indicate that incorporating multiple membrane regenerators, with different performance parameters and inlet and outlet contaminant concentration limits in a water network, facilitates the optimal use of freshwater. Thus, the inlet contaminant concentration limits were set at different levels in order to allow membrane regenerators varying options for contaminant treatment. The model that incorporated a variable removal ratio in scenario 3 proved to yield the optimal result for the illustrative example, as represented in Figures 4.10 and 11. The configuration, which demonstrates regeneration reuse and regeneration recycle within the water network, results in a 43.7% reduction in freshwater consumption,

a 50.9% reduction in wastewater generation and a 46% saving in the total annualised water network cost, as compared to scenario 1. Table 4.7 and Table 4.8 contain the design results of the ED and RO units respectively. Of note are the optimum removal ratios for both units, which are different from the fixed removal ratio of 0.7. Additionally, the results include the detailed design parameters for the units which result in the optimal use of energy and water. The statistics of the model for all the cases are shown in Table 4.10

Table 4-8: Optimal design results for electrodialysis unit in scenario 3

Variable	Value
N	50
$A \text{ (m}^2\text{)}$	54.4
$L \text{ (m)}$	0.8
$I \text{ (A)}$	12.5
$v \text{ (m/s)}$	0.01
$U \text{ (V)}$	30.2
$E^{spec} \text{ (J/s)}$	0.02
$E^{pump} \text{ (J/s)}$	0.004
$\Delta P \text{ (kPa)}$	16.3
$Q^{Fed} \text{ (t/h)}$	1.03
RR_e	0.8

Tables 4.8 and 4.9 contain the results of key design variables for both ED and RO units in scenario 3 under the variable removal ratio. The developed model was applied to the single contaminant effluent illustrative example and solved using BARON as the solver for LP and MINLP in all scenarios. It can be seen that the number of constraints increased from scenario 1 to scenario 2 due to the increasing number of integer, continuous and binary (0, 1) variables and consequently the huge number of constraints.

Table 4-9: Optimal design results for reverse-osmosis unit in scenario 3.

Variable	Value
N_m	10
P_F (kPa)	5.73×10^5
P_R (kPa)	5.33×10^5
ΔP_{shell} (kPa)	4.52×10^5
$\Delta \pi_{ro}$ (kPa)	1.63
P_{turb} (J/s)	3615.97
P_{pump} (J/s)	301.66
Q^{Fro} (t/h)	0.72
RR_r	0.65

The introduction of detailed design constraints for membrane regeneration units further increased the number of continuous and discrete variables, resulting in a significantly increased model size in scenario 3. The presence of binary and integer variables as well as nonlinear and logarithmic constraints rendered the model highly nonlinear. As a result, the model is classified as a mixed integer nonlinear program (MINLP). MINLP models are inherently difficult to solve and hence the CPU time required for the detailed model is high compared to both the base model and “black-box” models. This is displayed in Tables 4.10.

Table 4-10: Model characteristics for all cases

	Scenario1	Scenario2		Scenario3	
		Fixed RR	Variable RR	Fixed RR	Variable RR
No. of constraints	31	232	232	276	276
No. of continuous variables	68	185	187	222	224
No. of discrete variables	25	67	67	69	69
Tolerance	0	0.001	0.001	0.001	0.001

Figures 4.2 to 4.11 illustrate the optimal design configuration and flowsheets for all scenarios considered for the case study. Based on the results in Tables 4.7, it is

evident that Figures 4.10 and 4.11 present the best results. This indicates that setting the removal ratio as a variable gives the optimisation model the degree of freedom required to determine the true optimum conditions.

4.4 Illustrative Example Involving Multiple-Contaminants

Table 4.11 contains the limiting data for the second illustrative example, involving multiple effluent contaminants. Water from sources, including a freshwater source, is used to satisfy the demands of process water sinks, which include a wastewater sink. Process streams which require partial treatment are fed into the regeneration units to enhance their quality before being used in the sinks. As indicated in Table 4.11, five sources and five sinks are present. Two contaminants, namely, NaCl and COD, are identified for this case study. The available source flowrates and their contaminant concentrations, as well as the maximum allowable flowrates into sinks and their limiting contaminant concentrations, are specified in Table 4.11. The process and economic data presented in Tables 4.2, 4.3, 4.4, and 4.5 are maintained and used for the multiple contaminant effluent illustrative example in this section.

Table 4-11: Process data for water network

j	Flowrate (t/s)	Sources, j		i	Flowrate (t/s)	Sinks, i	
		Conc. (mg/L)				Max. conc. (mg/L)	
		NaCl	COD			NaCl	COD
1	0.247	0	600.34	1	0.388	34.22	34.22
2	0.040	30.02	30.02	2	0.040	0	60.03
3	0.028	0	120.07	3	0.160	0.37	20.41
4	0.861	498.28	498.28	4	0.861	0	54.03
FW	—	0	0	WW	—	600.34	600.34

4.4.1 Model Considerations for Illustrative Example

Table 4.11 contains the process data for the multiple-contaminant effluent illustrative example. Similarly to the single contaminant illustrative example, the multiple contaminant illustrative example involves five water sources, $j = \{j_1, j_2, j_3, j_4, j_5\}$, including the freshwater source, five sinks,

$i = \{i_1, i_2, i_3, i_4, i_5\}$, including the wastewater sink and two contaminants
 $co = \{co_1, co_2\}$

Explicit detailed descriptions of modified constraints for the multiple-contaminant effluent case study are presented as follows:

Mass and Concentration Balance for Regeneration Units

Constraints (4.42) to (4.44) are illustrative examples of the maximum allowable contaminant concentrations into the membrane regenerator units base on the process data in Table 4.11.

$$800 \geq \frac{\sum_{j=j_1}^{j_5} Q_j^{ed} C_{j,co_1}^x + Q^{de} C_{co_1}^{Ped} + Q^{ee} C_{co_1}^{Red} + Q^{fe} C_{co_1}^{Pro}}{Q^{Fed}} \quad (4.42)$$

$$3902 \geq \frac{\sum_{j=j_1}^{j_5} Q_j^{ro} C_{j,co_1}^x + Q^{dr} C_{co_1}^{Pro} + Q^{gr} C_{co_1}^{Rro}}{Q_i^z} \quad (4.43)$$

$$3902 \geq \frac{\sum_{j=j_1}^{j_5} Q_j^{ro} C_{j,co_2}^x + Q^{fr} C_{co_2}^{Pro} + Q^{gr} C_{co_2}^{Rro}}{Q^{Fro}} \quad (4.44)$$

Similarly, maximum allowable contaminant concentrations for the sinks, based on the data from Table 4.11, are illustrated by constraints (4.45) to (4.54).

$$34.22 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_1}^a C_{j,co_1}^x + Q_{i_1}^{ds} C_{co_1}^{Ped} + Q_{i_1}^{es} C_{co_1}^{Red} + Q_{i_1}^{fs} C_{co_1}^{Pro} + Q_{i_1}^{gs} C_{co_1}^{Rro}}{Q_{i_1}^z} \quad (4.45)$$

$$0.00 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_2}^a C_{j,co_1}^x + Q_{i_2}^{ds} C_{co_1}^{Ped} + Q_{i_2}^{es} C_{co_1}^{Red} + Q_{i_2}^{fs} C_{co_1}^{Pro} + Q_{i_2}^{gs} C_{co_1}^{Rro}}{Q_{i_2}^z} \quad (4.46)$$

$$0.37 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_3}^a C_{j,co_1}^x + Q_{i_3}^{ds} C_{co_1}^{Ped} + Q_{i_3}^{es} C_{co_1}^{Red} + Q_{i_3}^{fs} C_{co_1}^{Pro} + Q_{i_3}^{gs} C_{co_1}^{Rro}}{Q_{i_3}^z} \quad (4.47)$$

$$0.00 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_4}^a C_{j,co_1}^x + Q_{i_4}^{ds} C_{co_1}^{Ped} + Q_{i_4}^{es} C_{co_1}^{Red} + Q_{i_4}^{fs} C_{co_1}^{Pro} + Q_{i_4}^{gs} C_{co_1}^{Rro}}{Q_{i_4}^z} \quad (4.48)$$

$$600 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_5}^a C_{j,co_1}^x + Q_{i_5}^{ds} C_{co_1}^{Ped} + Q_{i_5}^{es} C_{co_1}^{Red} + Q_{i_5}^{fs} C_{co_1}^{Pro} + Q_{i_5}^{gs} C_{co_1}^{Rro}}{Q_{i_5}^z} \quad (4.49)$$

$$34.22 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_1}^a C_{j,co_2}^x + Q_{i_1}^{fs} C_{co_2}^{Pro} + Q_{i_1}^{gs} C_{co_2}^{Rro}}{Q_{i_1}^z} \quad (4.50)$$

$$60.03 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_2}^a C_{j,co_2}^x + Q_{i_2}^{fs} C_{co_2}^{Pro} + Q_{i_2}^{gs} C_{co_2}^{Rro}}{Q_{i_2}^z} \quad (4.51)$$

$$20.41 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_3}^a C_{j,co_2}^x + Q_{i_3}^{fs} C_{co_2}^{Pro} + Q_{i_3}^{gs} C_{co_2}^{Rro}}{Q_{i_3}^z} \quad (4.52)$$

$$54.03 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_4}^a C_{j,co_2}^x + Q_{i_4}^{fs} C_{co_2}^{Pro} + Q_{i_4}^{gs} C_{co_2}^{Rro}}{Q_{i_4}^z} \quad (4.53)$$

$$600.34 \geq \frac{\sum_{j=j_1}^{j_5} Q_{j,i_5}^a C_{j,co_2}^x + Q_{i_5}^{fs} C_{co_2}^{Pro} + Q_{i_5}^{gs} C_{co_2}^{Rro}}{Q_{i_5}^z} \quad (4.54)$$

4.5 Results and Discussions of the Multiple Contaminant Illustrative Example

This section reports on the application of the developed model to the multi-contaminant effluent illustrative example. In reality, wastewater streams present in process industries commonly contain more than one contaminant and hence the investigation of a multiple contaminant illustrative example is justified. The ED is formulated to remove only the ionic contaminant; hence the sequence of the constraints that specify the removal of contaminants in the ED and in the RO unit is paramount. Constraints (3.58) to (3.61), which represent the contaminant mass load around a mixing process preceding the regeneration units, the maximum load into the sinks as well as the mass balance constraints from the reject stream of the RO unit into the ED, are modified. Additionally, constraints (3.62) to (3.69), which represent the design equations of the ED unit, are also modified to cater for the operation of the ED unit, since the formulation is single ionic contaminant

specific. The RO unit, on the other hand, is capable of removing any or both of the contaminants. The contaminants to be removed by the RO unit are determined by the model. This section presents the results of the different scenarios considered under the multiple contaminant effluent illustrative example. A comparative analysis of scenarios is conducted and a detailed discussion of the results, the model characteristics and the regeneration cost analysis is presented.

4.5.1 Scenarios Considered

The illustrative example in this current work was applied to three scenarios and the results were compared.

Scenario 1 considers a base case mathematical model for water network optimization without membrane separation regenerators.

Scenario 2 presents a mathematical model for integrated water network optimisation using a “black-box” approach. This approach includes membrane regeneration units, however detailed design constraints of the regeneration units are omitted. The performance of the regeneration units are characterised by a variable removal ratio.

Scenario 3 considers a detailed mathematical model of the membrane regenerator units within a water network synthesis and optimization. The third scenario also uses a variable removable ratio framework.

The variable removal ratio formulation was chosen over the more rigid fixed removal ratio for scenario 2 and 3 because it has proven to be the better method for optimal operation of the regeneration units as determined through a water network superstructure optimisation (Yang et al., 2014, Buabeng-baidoo & Majozi, 2015, Mafukidze & Majozi, 2015). Recent research has demonstrated that models with fixed removal ratios do not give the optimisation the degree of freedom required to explore and select the best performance for the regeneration units (Yang et al., 2014, Buabeng-Baidoo & Majozi, 2015, Mafukidze & Majozi, 2015).

4.5.2 Results

Table 4.12 contains the optimal results for the illustrative example, “black-box” model, and detailed model. The results include the freshwater consumption, wastewater production, and total cost of water network for all scenarios.

Table 4-12: Summary of results for all scenarios based on case study

	Base Model	Blackbox Model	Detailed Model
Freshwater (t/s)	1.134	0.989	1.00
Freshwater savings %	-	12.8	11.6
Wastewater (t/s)	0.861	0.716	0.729
Wastewater saving %	-	16.8	15.3
Total cost (million \$)	56.9	48.7	50.9

The solution of the base model (scenario 1) indicated that the optimal freshwater requirement was 1.134 t/s, while the wastewater generation rate was 0.861 t/s. The total network cost was \$56.9 M. The optimal network configuration for the base case scenario is displayed in Figure 4.12.

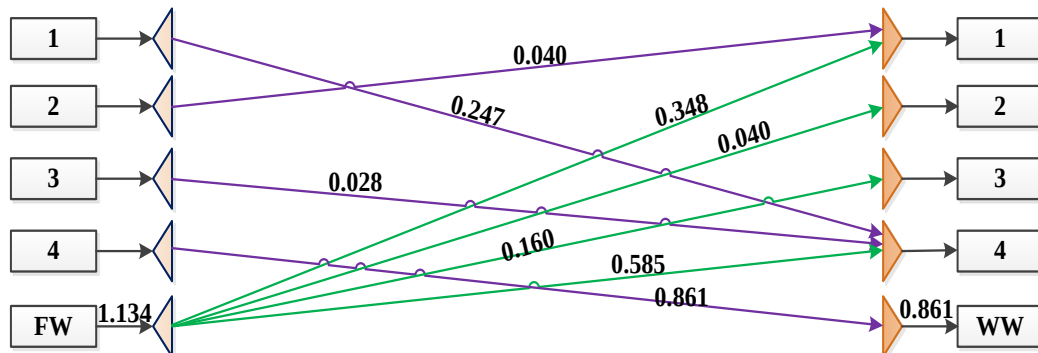


Figure 4.12: Optimum water network configuration for scenario 1 (No regeneration)

The “black-box” model approach yielded a requirement of 0.989 t/s freshwater with a corresponding wastewater production rate of 0.716 t/s. The total water network cost for this configuration is \$48.7 M. These figures translate to a 12.8%

reduction in freshwater consumption and a 16.8% reduction in wastewater generation when compared to the base case model (scenario 1). The “black-box” model also delivered a 14% saving in network costs as compared to the base case model. Figure 4.12 displays the optimal water network configuration for the “black-box” model.

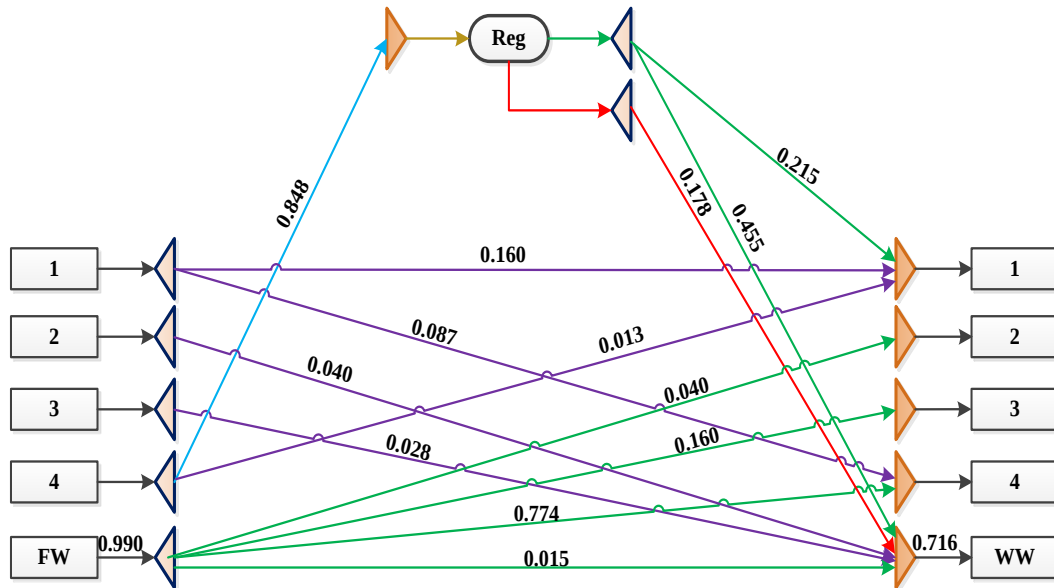


Figure 4.13: Optimum water network configuration for scenario 2 (Blackbox variable RR)

The detailed model identified a configuration requiring 1.00 t/s freshwater and which produces 0.729 t/s wastewater. The respective savings from the base case model are an 11.6% reduction in freshwater consumption and a 15.3% reduction in wastewater production. The total cost of the water network for the detailed model also was also reduced by 10.5% from that of the base case model. The optimal water network configuration for the detailed model is displayed in Figure 4.14.

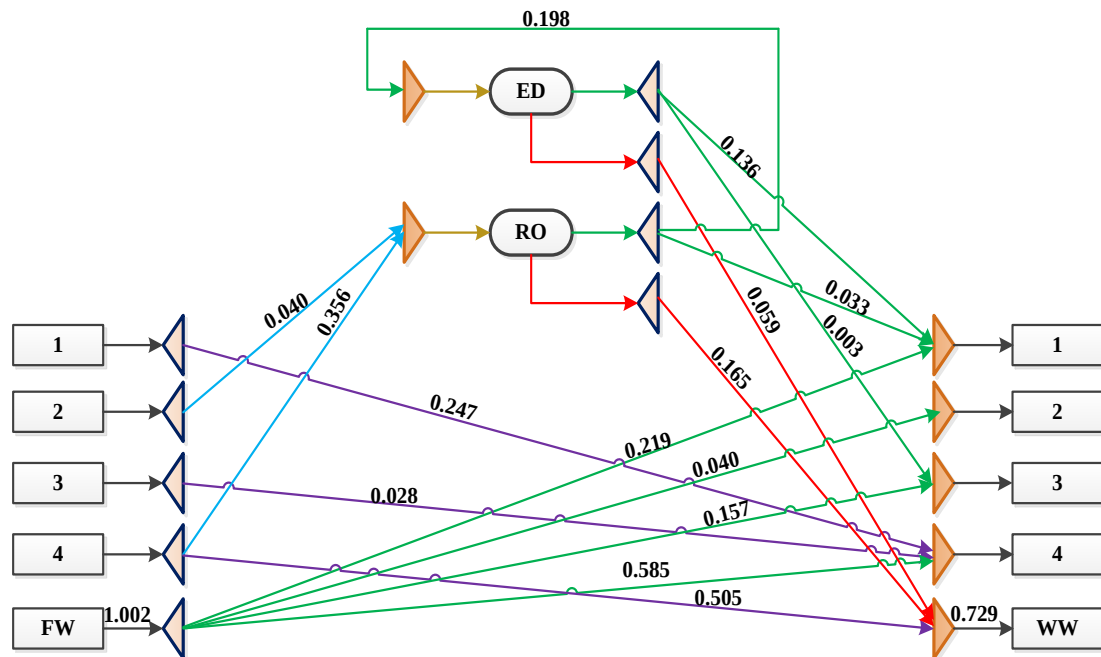


Figure 4.14: Optimum water network configuration for scenario 3 (Detailed variable RR)

The results showed that integrating membrane regenerator units within a water network superstructure is essential for water minimization. A comparative look at the results demonstrated that the “black-box” model obtained better results than the detailed model in terms of freshwater consumption and wastewater generation. The total water network cost was also lower for the “black box” scenario by 4.3%. The “black box” model, however, does not reflect all aspects of the problem as accurately as the detailed model. Specifically, the detailed model includes the purchasing cost of freshwater, the cost of wastewater treatment, the cost of wastewater regeneration and the associated piping and operating costs, whereas the “black box” model does not.

4.5.3 Discussion

The optimal water network configurations for scenarios 1, 2 and 3 are presented in Figures 4.12, 4.13 and 4.14, respectively. Table 4.12 shows that scenario 1 delivered the worst results since the quantity of water consumed and the cost of the water network was significantly higher than those of scenarios 2 and 3. Both scenario 2 and 3 yielded better results in terms of water consumption and the cost

of the water network. This shows that regeneration within a water network system is very important for the sustainable and cost effective use of water. Scenario 2, however, delivered the best results among the 3 scenarios as it required the least freshwater consumption, produced the least wastewater and identified a water network with the lowest cost. The results of scenario 2 are, however, deceptive and do not give a true representation of the water network cost. Additionally, scenario 2 does not offer the design opportunity and identification of the regeneration units, since they are characterised by the fixed removal ratio and a linear cost function. Further, the results are misleading as the uncertainty of the required types of regeneration units, which could range from membrane regeneration units to non-membrane regeneration units, will demand additional investigation. In order to ascertain the optimal solution between scenario 2 and 3, a further sensitivity analysis is conducted. The results are shown in Table 4.13.

Table 4-13: Summary of regeneration cost analysis

	Blackbox model		Detailed Model
	Estimated cost	True cost	
Total reg. feed (t/s)	0.848	0.848	0.747
Reg. cost (million \$)	0.099	3.68	1.573
Total cost (million \$)	48.7	52.2	50.9

Table 4.13 contains the results of the regeneration cost analysis for scenarios 2 and 3. The total feed into the regeneration units, which are based on the optimal design configurations of Figures 4.13 and 4.14 are represented together with the respective regeneration costs of scenario 2 and 3. The regeneration cost of scenario 2 is divided into estimated cost and true cost. Estimated cost represents the cost of regeneration and the total water network in scenario 2, whereas true cost represents the cost of regeneration and the total water network which would arise if the same amount of contaminated water was fed into the detailed model. Table 4.13 shows that the estimated cost of regeneration for the “black-box” model is lower than the true cost. Specifically, the estimated water network cost shows a deviation of up to 7% from the true cost. Thus, in actuality, Table 4.13

indicates that scenario 3 presents the best solution and the optimal configuration, which is shown in Figure 4.14. This is demonstrated by a 57.3% savings in regeneration and energy cost, and a 2.5% saving in the total water network cost in comparison with scenario 2.

4.5.4 Model Characteristics

Important model characteristics for all scenarios are presented in Table 4.13. The number of constraints, continuous variables, discrete variables and computational times increases with the size of the models.

Table 4-14: Summary of model characteristics for all scenarios

	Base case	Blackbox Model	Detailed Model
No. of constraints	91	139	312
No. of continuous variables	73	117	241
No. of discrete variables	25	43	67
Tolerance	0	0.001	0.001
Time (s)	0	123	59875

Scenario 2 took approximately 2mins, whereas the detailed model requires over 16 hours to find a feasible solution. The higher computational time of the detailed model is as a result of the nonlinear nature of the water network model. Tighter bounds were however imposed on certain variables of the regeneration units to aid convergence. The bounds imposed on the ED unit model included number of cell pairs, linear flow velocity, stacks length, and recovery rate etc. The bounds on the RO regeneration unit included but not limited to number of reverse osmosis modules, permeate pressure and retentate pressure. Freshwater intake and wastewater generated flowrates for scenario 1 were taken as upper bounds for scenario 2 and 3. This was done to ensure that the freshwater intake and wastewater discharge for scenario 2 and 3 did not exceed scenario 1 as there would be no need for regeneration. The complexity of the detailed model results in longer computational time. Insightful mathematical techniques are therefore needed to reformulate the model for easier convergence. Powerful computers and

robust mathematical solvers are needed to help the optimization and computation of MINLP problems.

Table 4-15: Optimal design results for ED unit in scenario 3 (Detailed Model)

Variable	Value
N	100
$A \text{ (m}^2\text{)}$	65
$L \text{ (m)}$	0.7
$I \text{ (A)}$	14.5
$v \text{ (m/s)}$	0.04
$U \text{ (V)}$	40.2
$E^{spec} \text{ (J/s)}$	0.04
$E^{pump} \text{ (J/s)}$	0.006
$\Delta P \text{ (kPa)}$	20.3
RR_e	0.7

Table 4-16: Optimal design results for the RO unit in scenario 3 (Detailed Model)

Variable	Value
N_m	20
$P_F \text{ (kPa)}$	6.63×10^5
$P_R \text{ (kPa)}$	5.32×10^5
$\Delta P_{shell} \text{ (kPa)}$	6.87×10^5
$\Delta \pi_{ro} \text{ (kPa)}$	3.00
$P_{turb} \text{ (J/s)}$	4615.97
$P_{pump} \text{ (J/s)}$	601.66
RR	0.84

Tables 4.15 and 4.16 contain the results of key design variables for both ED and RO units in scenario 3 under the variable removal ratio for the detailed model. The optimal variables presented can be used for optimal design of both ED and RO units for maximum water output and minimum energy usage.

4.6 Conclusion

In this chapter the developed mathematical model in Chapter 3 is applied to two illustrative examples from literature to demonstrate its applicability. The first illustrative example involves effluent with single contaminant whereas the second illustrative example involves effluents with multiple contaminants. The results showed that integrating detailed models of ED and RO units within a water network superstructure directly influences water consumption, design configuration, cost representation of regeneration units as well as optimal design parameters of regeneration units. The results obtained in this chapter showed that optimization of detailed regeneration units within a water network can significantly improve wastewater management within the process industry. The results also showed that synthesis of regeneration units within water network superstructure yields optimal operating parameters that can be used to design regeneration units for minimal energy usage as well as accurate cost representation. In conclusion the work presented in the chapter can be used as one of the tools towards attaining the water energy nexus goals.

4.7 References

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Case Study

5.1 Introduction

In this chapter, the mathematical model which was developed in Chapter 3 is applied to an industrial case study concerning a power utility plant in South Africa. The objective of this chapter is to demonstrate the merits of using an integrated water network approach to achieve sustainable water usage in the process industry through water minimization. As in any water minimisation project, there is a need to identify the main water producing and using units as well as to obtain various data pertaining to plant operation. This chapter therefore includes the methods of data acquisition and validation which were used in order to obtain the necessary information for the case study in question. The data includes the power plant's rate of water consumption as well as the maximum permissible concentrations of contaminants in each process unit's effluent stream. Following this, the current consumption of water in the power plant is compared to that determined through the optimization model, considering direct reuse and recycle and regeneration reuse and recycle opportunities. As was done in Chapter 4, optimization was applied via both the "black-box" approach and the detailed regeneration unit approach. The results are then compared to the current-practice process water data to obtain the optimal solution for the case study in terms of freshwater consumption, wastewater generation and overall water network cost.

5.2 Data Gathering and Validation

The Kriel power station is a coal fired power utility plant based in the north eastern province of South Africa, Mpumalanga. Kriel power station generates about 3000 MW of electricity to meet the increasing demand of the growing population in South Africa. The plant receives raw water, for both industrial and

domestic purposes, from the Vaal and Usutu water schemes, which also supply water to many towns and cities in South Africa. However, the Kriel facility currently exceeds its water consumption design target by 10-15Ml/d on average (Kriel WAF Report, 2014). This does not bode well for the company and the country from a business point of view as well as a sustainability point of view, considering that South Africa is a water scarce country. There is therefore a need to employ sustainable process integration techniques for water minimisation within the power utility plant.

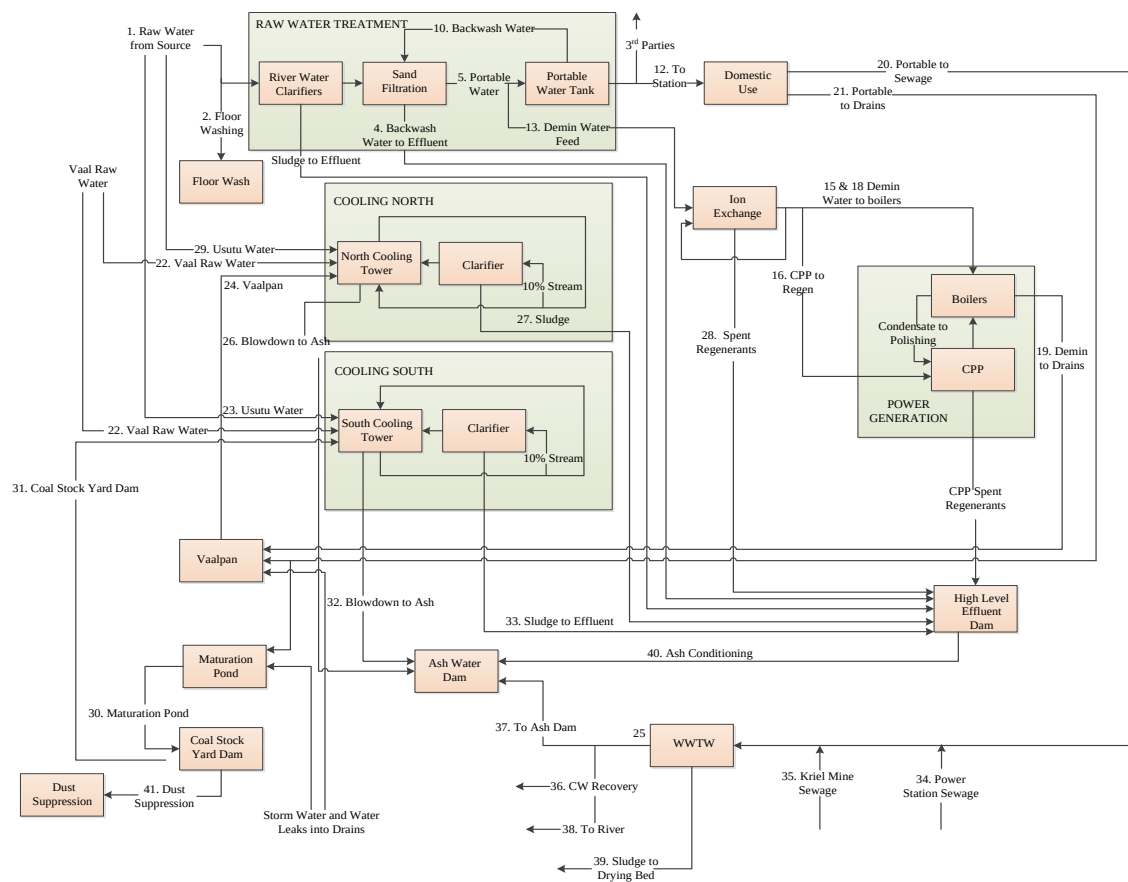


Figure 5.1: *Current Water utilisation network flowsheet at Kriel Power plant*

Figure 5.1 displays the water utilisation network flowsheet for the power station. The Usutu dam and Vaal river are the two sources of water supply to the power plant and 3rd parties. 3rd parties are communities or industries that use same water supply as the power plant. Ash dam within a power plant is basically a barrier constructed to contain ash slurry. Ash dam is a place to safely store ash which as a

by-product produced during the combustion process. Just like the ash dam, effluent dam is a safely constructed barrier to contain effluent. Demineralized water is one of the crucial types of water within a power plant which is used for steam generation in a boiler. Hardness, TDS and TSS levels and conductivity are kept at permissible limits. A cooling tower is a heat rejection device which extracts waste heat to the atmosphere through the cooling of a water stream to a lower temperature. The wastewater treatment works within a power plant treats wastewater to environmental acceptable levels before being discharged into the environment.

Based on the water flow diagram presented in Figure 5.1, process units are identified and grouped as sources and sinks. The results of this classification are contained in Table 5.1. It is worthy of mention, however, that some process units may serve as both sources and sinks simultaneously. A typical example of such a unit is the cooling tower, which has a demand for water and also generates water in a form of blowdown water. The raw water sources are classified as variables because their flowrate, together with other model variables, will be minimized by the model.

Table 5-1: Identified sources and sinks for the case study

Unit Operations	Sources	Sinks	Variables
Usutu Raw Water			X
Vaal Raw Water Supply			X
Floor Washing		X	
3 rd Parties		X	
Sand Filter Backwash Water		X	
Dirty Sand Filter Backwash Water	X		
Power Station Potable Water Leaking into Drains (Bathrooms etc.)		X	
Power Station Potable Water Leaking into Drains	X		
Power Generation: Demin Water		X	
Power Generation: Demin Water to Drains-Mostly Tank Overflows	X		

Power Generation: CPP Spent Regenerants	X	
Ion Exchange: Spent Regenerants	X	
Effluent Dam	X	
North Cooling Tower	X	X
South Cooling Tower	X	X
WWTW	X	
Ash Dam/Ash Conditioning		X
Dust Suppression		X
Vaalpan – Mostly from Process Unit Leak	X	

Table 5.2 contains data pertaining to the flowrates and contaminant concentrations available from sources as well as the maximum flowrates and permissible concentrations into sinks, including the wastewater sink. The process data comprises of eleven water sources and ten water sinks including the freshwater sources and wastewater sink. The respective flowrates and contaminant concentrations from sources as well as the maximum allowable flowrates and contaminant concentrations into sinks are specified. The freshwater sources and wastewater sinks are only represented by their contaminant concentrations and maximum allowable contaminant concentrations respectively. Their flowrates are presented as unknown and variable because the main objective of this study is to minimise freshwater consumption and wastewater generation. Based on the process data, a single contaminant (H_2SO_4) is identified and presented for the case study.

Table 5-2: Basic data for sources and sinks

Sources				Sinks			
No	Name	Flowrates m^3/d	Conc. Mg/l	No	Name	Flowrates m^3/d	Conc. Mg/l
1	SF backwash	444	48	1	F. washing	2203	43
2	PS to Drains	1890	58	2	3 rd Parties	3000	45
3	PG to Drains	3412	0	3	SF backwash	444	45

4	CPP Regents	4094	0	4	PS Potable	3000	45
5	Spent Regents	1039	127	5	PG Demin	6824	0
6	NC Tower	3177	2548	6	NC Tower	46389	862
7	SC Tower	6467	2548	7	SC Tower	46389	130
8	Effluent Dam	1400	6369	8	Ash Dam	11044	6369
9	WWTW	50	249	9	D Suppression	400	2548
10	Vaalpan	800	732	10	Waste Dam	—	10000
11	Freshwater	—	45				

5.3 Scenarios Considered

Three scenarios are considered for the case study and the results are compared against the current water utilisation data of the power utility plant. Scenario 1 employs a mathematical model which includes process integration techniques and considers opportunities for reuse and recycles. The objective of Scenario 1 is to minimise freshwater consumption, wastewater generation and the total combined costs associated with freshwater intake and wastewater treatment.

The second scenario considers a mathematical model with a regeneration unit that is able to remove contaminants from streams to produce quality water that is more amenable for reuse and recycle. The regeneration unit in this scenario is characterised as a “black-box” model. This is because the cost of regeneration is represented by an assumed linear function of the quantity of water fed to the regeneration unit. As per Scenario 1, the results of Scenario 2 are compared against the current process water network at the power station in the areas of freshwater consumption, wastewater generation and the total water network costs, including combined associated costs for regeneration, freshwater purchase and wastewater treatment.

Scenario 3 considers a detailed model of the regeneration units within a water network superstructure. As per Scenarios 1 and 2, the idea behind employing the detailed model is to perform a comparative analysis in terms of freshwater consumption, wastewater generation, and water network cost, where the costs pertaining to the regeneration units are expected to be more accurate than in Scenario 2.

Based on the case study and process data reported in Table 5.2, certain considerations are made in order to cater for the reuse of treated wastewater effluent, the allowing of the interchange of blowdown water between the two cooling towers and the use of any water for floor washing operations. The current process water network at the Kriel power utility plant does not include reuse of treated wastewater, the interchange of blowdown water between cooling towers and the use of any water from the process units for floor washing. The two cooling towers at the Kriel power utility plant operate at different cycles of concentrations (CoC), with the south cooling tower operating at a lower cycle of contaminants. It is therefore important to allow for the interchange of blowdown water between the north and the south cooling towers in order to draw on the merits of sustainable water usage.

5.4 Results and Discussions

Table 5.3 shows the optimal results for the case study for Scenarios 1, 2 and 3 as well as the current process water utilisation data for the Kriel power utility plant. The results include the plant's freshwater consumption, wastewater generation, and total water network cost, which is comprised of freshwater purchase, wastewater treatment and regenerator unit cost. Based on the water utilisation report, the power utility plant consumes up to 119693 m³/d freshwater, produces 10000 m³/d wastewater and spends R719616/d on freshwater purchase and wastewater treatment. The design configuration of the current water network at the power plant is presented in Figure 5.1. The data for the current water utilisation at the power plant will serve as a reference of comparison for Scenarios 1, 2 and 3.

Figure 5.1 presents the current water utilisation network at the Kriel power plant. The current utilisation does not take into account water reuse and recycle, regeneration reuse and recycle opportunities hence freshwater water consumption and wastewater generation are quite high. Figure 5.2 presents optimal water network configurations when direct reuse and recycle opportunities are explored. Figure 5.3 presents water network configuration when water reuse, recycle, and regeneration reuse and recycle opportunities is explored. The regeneration units in

this presentation are however characterised by linear cost functions hence they are black-box representation. Figure 5.4 presents the water network configuration which incorporates detailed models of the regeneration units when reuse, recycle and regeneration reuse and recycle opportunities is explored.

Table 5-3: Optimal results for all scenarios based on case study

	Current Practice	Direct Reuse	Black-box	Detailed
Freshwater m ³ /d	119693	102718	96920	97290
FW savings %		14.2	19	18.7
Wastewater m ³ /d	10000	5789	0	1760
WW savings %		42	100	82.4
Total cost (In Rands/d)	R 719616	R646480	R588129	R597419
% savings in cost		10.2	18.3	16.9

Scenario 1, which involves direct reuse based on process integration techniques, results in a freshwater requirement of 102718 m³/d, a wastewater production rate of 5789 m³/d and an annual cost of R646480/d for freshwater purchase and wastewater treatment. This translates to a 14.2% reduction in freshwater consumption, a 42% reduction in wastewater production and a 10.2% reduction in the total water network cost when compared to the current water process data at the Kriel plant. The optimal water network design configuration for Scenario1 is shown in Figure 5.2.

The results of the black-box model indicated a freshwater consumption of 96920 m³/d, zero wastewater production and an annual cost of R588129/d for freshwater purchase and wastewater regeneration. When compared to the current water process data at the Kriel power plant, this translates to a 19% reduction in freshwater consumption, a 100% reduction in wastewater generation and an

18.3% reduction in the water network cost. The optimal design configuration for Scenario 2 is presented in Figure 5.3.

Scenario 3, which considers the detailed models of the regeneration units within a water network superstructure resulted in a freshwater consumption of 97290 m³/d , a wastewater production rate of 1760 m³/d and a total water network cost of R 597419/d. This translates to an 18.7% reduction in freshwater consumption, an 82.4% reduction in wastewater generation and a 17% reduction in overall water network cost when compared to the current practice at the Kriel power utility plant. The optimal design configuration for Scenario 3 is shown in Figure 5.4.

Comparative analysis of the optimization results indicates that there are merits in adopting an integrated approach for sustainable water use in the process industry, using reuse and recycle and regeneration reuse and recycle. It is evident that adopting any of the process integration techniques from Scenarios 1, 2 and 3 will yield better results as compared to the current water utilisation process at the power utility plant. It is also interesting to note that Scenario 2, which includes the “black-box” model, appeared to present the best optimal results compared to Scenarios 1 and 3. However, the results could be misleading as the cost of regeneration for the “black-box” model is based on a linear expression (Chew et al., 2008 and Tan et al., 2009). This approach does not give an accurate representation of the costs of energy consumption and those associated with the membrane system. Additionally, the black-box approach does not give an opportunity to identify the type of regenerator unit and its design considerations.

The results presented by the detailed model are considered to be the best optimal results compared to the base case and the three scenarios. This is because the results provide an accurate representation of the regeneration units and the overall water network cost.

5.4.1 Model Characteristic

Table 5.3 contains important model characteristics for Scenarios 1, 2 and 3. These include the number of constraints, the number of continuous variables and the number of discrete variables. Additionally, the required computational time for the solution of each scenario is presented.

Table 5-4: Model characteristics for all scenarios

	Direct Reuse	Black-box	Detailed
No. of constraints	283	350	500
No. of continuous variables	244	309	445
No. of Discrete variables	110	140	181
Tolerance	0	0.01	0.01
CPU Time (s)	0.063	17.780	3280

It can be seen that the number of constraints, continuous variables and discrete variables increases as the size of the models increase. This in turn results in the increased computational intensity required to solve the models. The direct model, which is the model with the least number of constraints, discrete variables and continuous variables, required less than a second to converge, whilst the black-box model required just over 17 seconds to solve. The detailed model required over an hour to converge due to the presence of bilinear, nonlinear, logarithmic, exponential and integer terms. This rendered the model a mixed integer nonlinear programme (MINLP). MINLP models are highly nonlinear and inherently computationally intensive. The model was solved using the branch and reduced algorithm solver (BARON) in GAMS.

Table 5-5: Optimal design variables for ED unit for the detailed Model

Variable	Value
N	50
$A \text{ (m}^2\text{)}$	60
$L \text{ (m)}$	0.7
$I \text{ (A)}$	14.5
$v \text{ (m/s)}$	0.4
$U \text{ (V)}$	38.2
$E^{spec} \text{ (J/s)}$	0.4
$E^{pump} \text{ (J/s)}$	0.023
$\Delta P \text{ (kPa)}$	20.3
RR_e	0.88

Table 5-6: Optimal design variables for the RO unit for detailed model

Variable	Value
N_m	20
$P_F \text{ (kPa)}$	6.63×10^5
$P_R \text{ (kPa)}$	4.14×10^6
$\Delta P_{shell} \text{ (kPa)}$	2.02×10^6
$\Delta \pi_{ro} \text{ (kPa)}$	3.00
$P_{turb} \text{ (J/s)}$	4715.97
$P_{pump} \text{ (J/s)}$	501.66
RR	0.75

Tables 5-5 and 5-6 present optimal design variables for the ED and RO units for scenario 3. These results can be used to design ED and RO units for maximum water output and minimum energy usage.

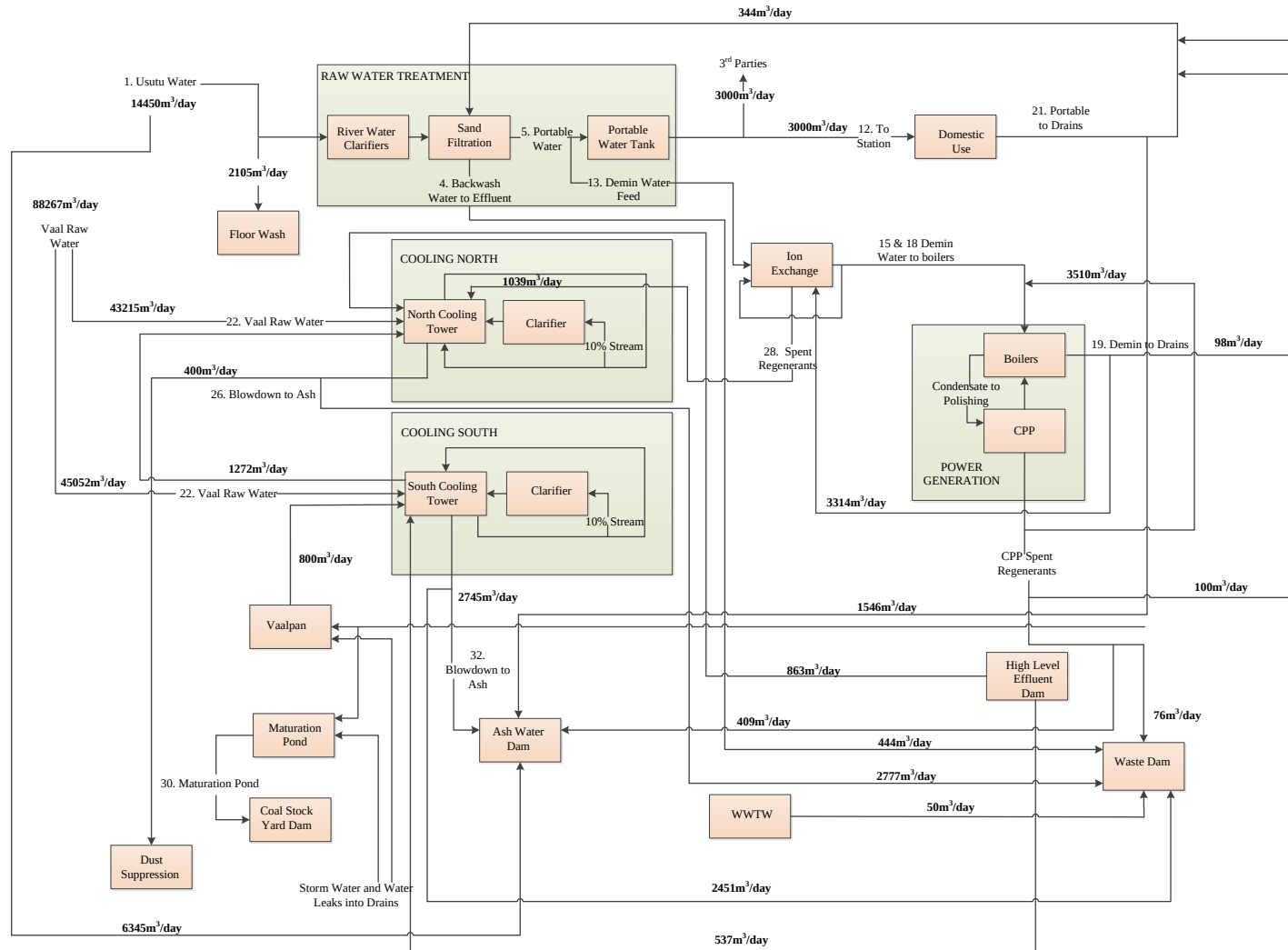


Figure 5.2: Optimal water network configuration for Scenario 1 (Direct reuse and recycle)

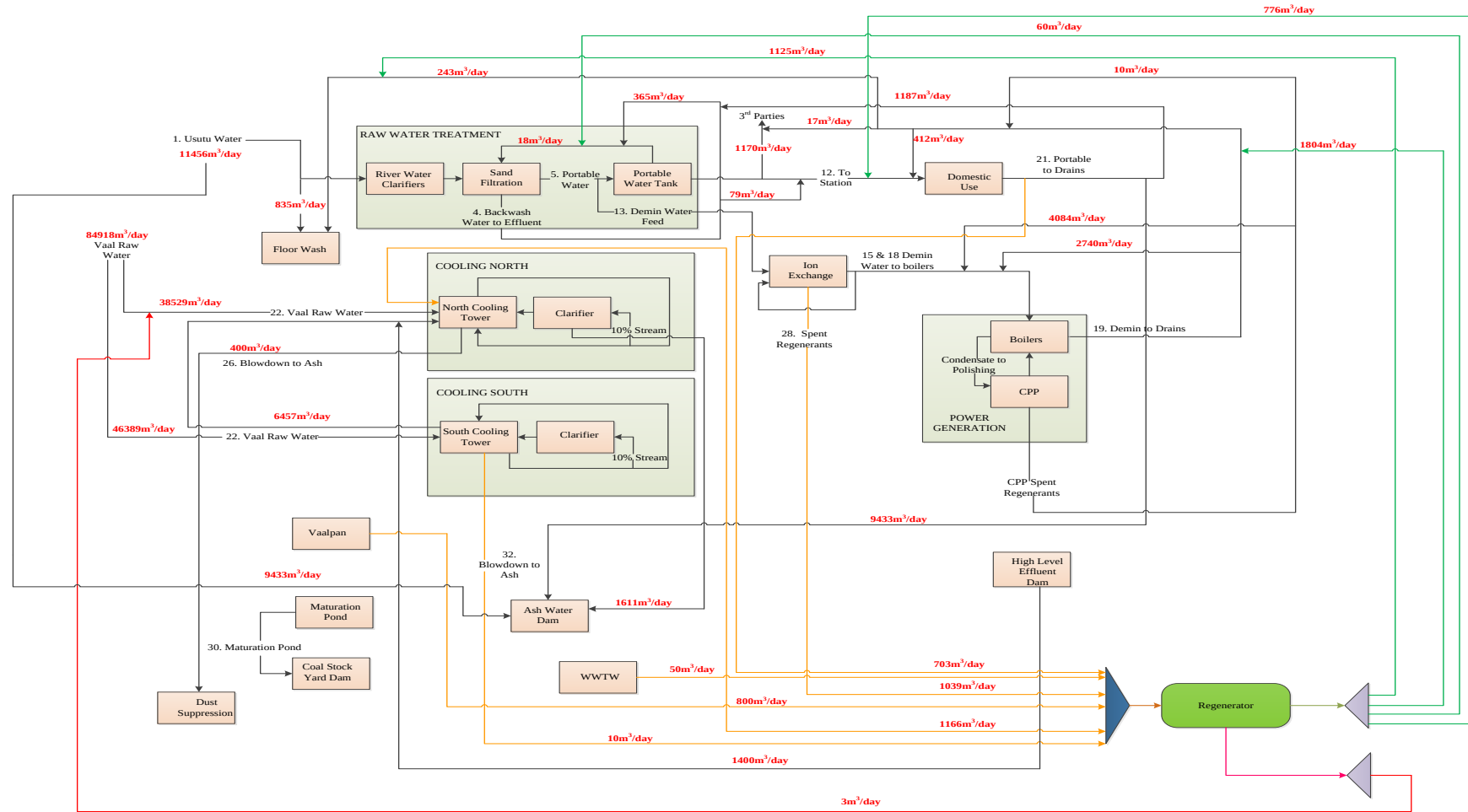


Figure 5.3: Optimal water network configuration for scenario II (Black-box Model)

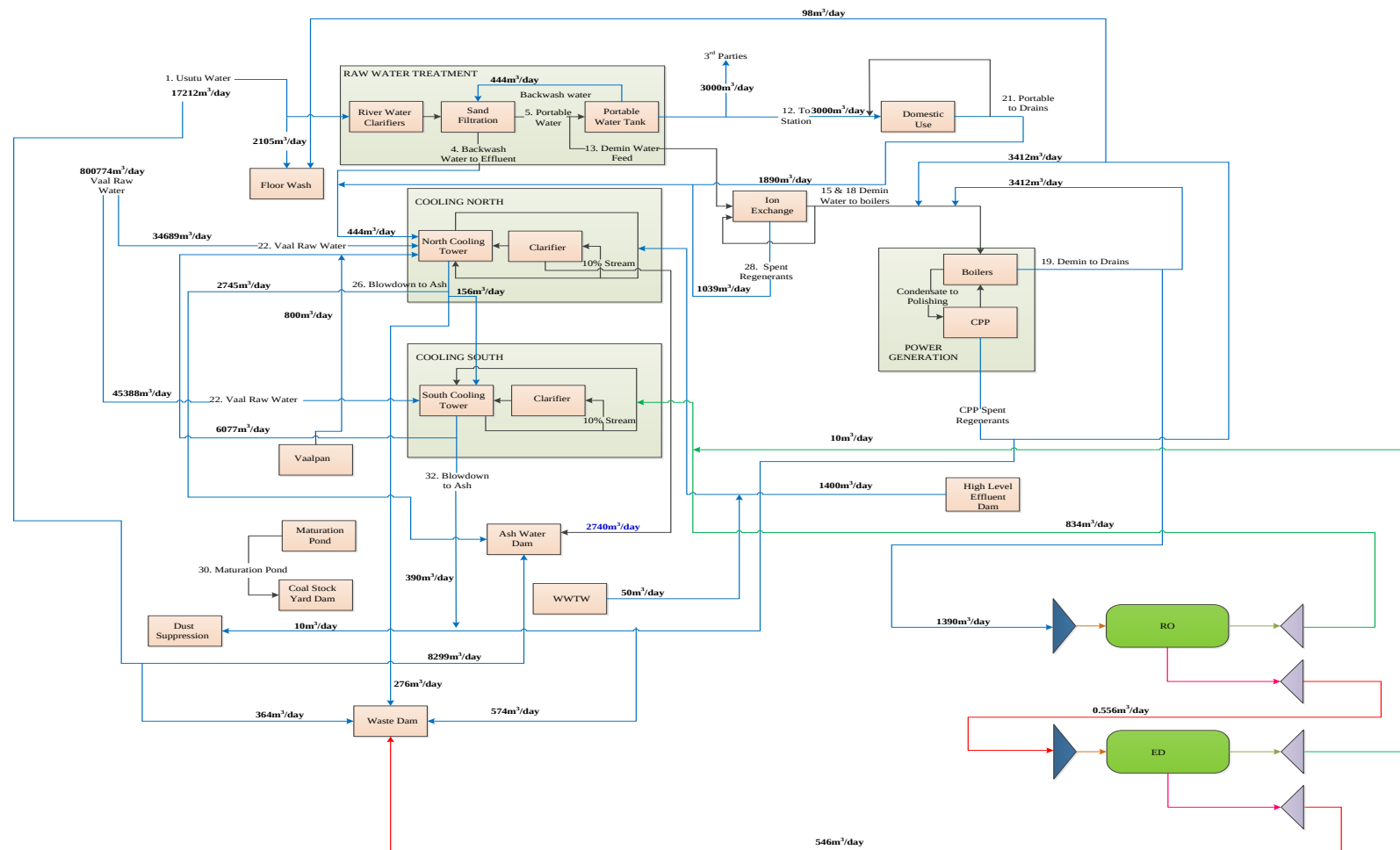


Figure 5.4: Optimal water network configuration for scenario III (Detailed Model)

The findings from the optimisation of the Kriel power utility water network show that Scenarios 1, 2 and 3 provide better operating schemes in terms of freshwater consumption, wastewater production and total water network cost. Scenario 3, being the optimal solution, will yield important benefits to the power plant if its operating scheme is adopted.

The Kriel power utility plant is reported to exceed its design water consumption target by 10000-15000 m³/d. This is a result of poor coal quality, the consequences of which are the decrease in quality of the generation cycles. Additionally, the poor freshwater quality results in lower cycles of concentration (CoC) and a higher make up water requirement. Other factors include the poorly managed infrastructure, which results in leakages, the lack of reuse of treated wastewater and the interchange of blowdown effluent between the north and south cooling towers.

The current model in Scenario 3 accounts for the reuse of treated wastewater and interchange of blowdown water between the north and south cooling towers and other process units requiring water. Additionally, the floor washing, which was previously restricted to water from the Usutu water source, is now at liberty to use any water from other sources that the optimisation deems fit. If the optimal results in Scenario 3 are adopted by the power plant, an 18.7% reduction in freshwater consumption and an 82.6% reduction in wastewater production may be realised. Additionally, a reduction of up to 14.2% in the total water network cost may be achieved. Included in the optimal water network design is a wastewater sink/dam. Unlike the effluent dam or ash dams, the wastewater sink is incorporated with consideration to the environmental department effluent discharge limits. This implies that bounds are set on the maximum concentration of contaminants in wastewater which is discharged to the dam. This is to ensure that effluent into the wastewater sink meets environmental discharge limits before being discharged. Incorporating a wastewater sink is a sustainable way of disposing toxic effluents into the environment without exceeding the environmental protection effluent discharge limits. This does not only aid sustainable process practices, it also

serves to guide the plant against fines which may arise due to the discharge of toxic effluent.

It is also important for the plant to invest in repairing and maintaining ailing infrastructure in order to prevent or recover water losses due to leakages. Based on the evidence presented in this chapter, it is important to apply process integration techniques as a tool for sustainable resource conservation in process design, retrofitting and operation by emphasising the unity of the process. The optimisation results have yielded optimal process water network designs, as shown in Figure 5.4, which can lead to minimum freshwater usage, minimum wastewater generation and the minimisation of the cost associated with these in terms of freshwater purchase, wastewater treatment and regeneration cost.

5.1 Conclusion

In this chapter the developed mathematical model in Chapter 3 is applied to an industrial case study involving a power plant to demonstrate its applicability. The results showed a savings of up to 18.7% freshwater consumption, 82.4% wastewater reduction and up to 17% savings on the overall total water network cost. The optimal water network configuration is also presented to showcase the merits of integrating detailed models that describes the design and operation of ED and RO units within a water network superstructure.

5.5 References

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RECOMMENDATIONS

6.1 Introduction

This chapter discusses the limitations of this work and recommends areas for considerations in future work. Computational challenges, as well as handling problems of complex MINLP problems are discussed. Recommendations are made for future work to consider multi-contaminant formulation. The work should also be extended to include other membrane and non-membrane regenerators. Considerations are made on optimization under uncertainty as well as preprocessing techniques to reduce computational time.

6.2 Parameter Values of Regeneration Units

This section deals with application of parameter values to detail design constraints of the regeneration units and their general implications to the work.

6.2.1 Parameters of ED Design Model

Most of the parameters applied to electro dialysis unit in the case study are adopted from Lee et al. (2002) and Tsiakis and Papageorgiou (2005). Some of the parameters are contaminant specific and are mostly determined experimentally. Sodium chloride is the ionic contaminant and its parameter values are as in Lee et al. (2002) and Tsiakis and Papageorgiou (2005). Parameters such as the limiting current density constant, anionic and cationic membrane resistance are all contaminant specific values. Electrical conductivity, which is concentration dependant was adopted from Lee et al. (2002) and Tsiakis and Papageorgiou (2005) because it should be determined experimentally. Nezungai and Majozi (2016) conducted a sensitivity analysis on the current density constant of an ED unit. Their analysis showed a deviation of up to 10% from base value of 25000 reported in Lee et al. (2002) and Tsiakis and Papageorgiou (2005). Nezungai and Majozi (2016) reported that the deviation did not have an impact on the financial

estimation on the cost of the ED unit. However, a 10% deviation in parameter accuracy could lead to 60% deviation in pressure drop of the ED unit from the optimal value. A 60% in pressure drop of the ED unit deviation could drastically change the optimal design of the ED unit. Nezungai and Majozi (2016) conducted similar analysis on the other current density constant and observed similar 10% deviation from the base value. Due to material impact on the design structure of the ED unit it is recommended that parameters are calibrated by conducting experiments on the types of contaminants and solution profile of the case study.

6.2.2 Assumptions in the ED Model Formulation

In formulating the ED design model, assumptions were made to describe the feed solution properties, hardware dimensions and operating conditions. Assumptions made among others were the following:

- i. Diluate and concentrate cells are geometrically similar with identical flowrates
- ii. The unit is operated in a co-current flow
- iii. Equal diluate and concentrate flowrates

Brauns et al. (2009) argues that the above assumptions limit the applicability of the model in individual cases and suggest there should be flexibility for the ED unit orientation in order to explore other opportunities.

6.2.3 Parameter Values for RO Unit

Parameter values for design configurations such as length of fibre, outer and inner radius and water permeability constant were used in modelling the reverse osmosis model. These parameters were adopted from Khor et al. (2011) and based on the feed solution characteristics and design configuration of the hollow fibre reverse osmosis module. There is a possibility that these parameters could vary depending on the case study and wastewater profile. Additionally, treating some of the parameters as variables could improve the optimal design of the RO membrane unit.

Treating some of the parameters as variables will lead to increased number of variables in the model. This will lead to increase feasible search space, which in turn will lead to model complexity and high computational intensity.

6.3 Model Structure

Poorly formulated model structure can lead to complications such as computational intensity, solver failure, unbounded solutions, infeasibility and implausible optimal solution.

Solver failure occurs when a model is applied to a wrong solver, magnitude of parameters are of differing degrees to the configuration of the solver leading to numerical difficulties or ill conditioning of the model. Solver failures may also be caused by degeneracy-induced cycling. Degeneracy occurs when basic variables are equal to zero and therefore the model become redundant. Cycling occurs when the model becomes “stuck” and iterates excessively at a single point.

Ill-structuring of the model can also lead to implausible optimal solution, where the model reports optimal solution however, upon checking the results values of variables appear to be impractical. This is often as a result of poor constraints formulations, errors in assigning parameter values, errors in coefficient estimation as well as algebraic errors.

In order to overcome the difficulties due to ill model formulations, it is essential to follow thorough model verification techniques. Model verification deals with systematic checks on the model to determine whether the model accurately represents the conceptual description of what supposed to present. The techniques include structural checking, a priori degeneracy resolution scheme, scaling, addition of artificial variables, introduction of upper bounds, addition of marginal values and row summing.

Structural checking involves analytical and numerical analysis of the model. Analytical analysis involves observation of parameter values to eliminate incorrect parameter estimation, avoid infeasibility, avoid forcing variables to zero and reduce redundant constraints. Numerical analysis is done by testing the

homogeneity of the units. A priory degeneracy resolution scheme relates to adding small numbers to the right hand of the equation to avoid redundancy. This can be done accurately by informed knowledge of marginal values. Scaling is important to eliminate disparity between parameters, variables, and equations. It can also be performed on the objective function. Artificial variables are added to a model to obtain feasible solution.

6.4 Computational Challenges

Within the realm of process optimization for water network systems, the presence of nonlinear and nonconvex terms poses a serious computational challenge. The inclusion of detailed regeneration units within the water network increased the complexity of model and rendered it highly nonlinear. This consequently increased the computational time required to solve the model as shown in Tables 4.6 and 4.13.

The computational time of the detailed model increases when the removal ratio is set as a variable. This is as a result of increased in model complexity with variable removal ratio framework. Computational intensity might not be a problem for design problems such as the work presented in this thesis since once a solution is obtained the computational time becomes irrelevant. However, in models that are formulated for scheduling in batch processes, time is an important constraint. It is therefore essential to improve computational time by adopting solution strategies such as piecewise-affine relaxation schemes, imposing of tighter bounds on variables etc. (Khor et al., 2014). Some optimization solvers do not report pi values which shows the sensitivity of variables on the solution. Most solvers used in GAMS report on marginal values which shows the sensitivity of parameters on the objective value to a particular variable. Inspection of the marginal values showed that most variables within the regeneration units exhibit marginal values greater than zero. This inherently implies that those variables that exhibit marginal values greater than zero are critical and important to the optimization problem.

6.5 Pre-Processing

Pre-processing involves the steps taken before solving a model in order to reduce computational intensity and achieve a better result. It is evident that in this work the computational time increases with the complexity of the model. It is therefore essential to consider strategies such as decomposition of the model. This method gives the model computational and organizational advantage. It breaks the original model into sub-problems which become easier to solve. Decomposition of models also gives convexity and sparsity which gives organization sense to some engineering problems. Other preprocessing steps includes the introduction of tight bounds to key variables, application of exact linearization techniques to nonlinear terms and reformulation of model constraints to their simplest form to avoid redundancy.

6.6 Multiple-Regenerators and Contaminants

The work presented in this work considers multiple membrane regenerators of ED and RO units, there are, however, different types of membranes based on their separation mechanism and type of contaminants separated. Generally effluent from the process industry contains multiple contaminants that are beyond the scope of the ED and RO units presented in this work. It is therefore imperative to formulate a model that incorporates other membrane regenerators that can handle contaminants that cannot be handled by the ED and RO units and also serve as pre-treatment to other units. The ED formulation in this work is limited to a single contaminant. It is therefore important for future work to consider formulations of ED models that can cater for multiple ionic contaminants.

Concentration polarization and membrane fouling are identified as the two major factors that affect the efficient operation of membrane separation units. Concentration polarization relates to the accumulation of solute species at upstream surface of the membrane (Delaney & Donnelly, 1977). Concentration polarization can be alleviated by operating the membrane separation system at high velocity flowrate that is if the system can withstand high velocity flowrates.

Membrane fouling involves the adsorption and trapping of particles present in the wastewater on the surface of the membrane material. The foulants affects the solute permeability and flux and severely affects the economic and practical implications of the membrane process (Yan-jun, 2000). Future research should focus on including fouling resistance models within the detailed regenerator models in order to increase the life span of the membrane materials.

6.7 Developing of Meaningful Optimization Techniques

There is a need for future work on computation and modelling of water network synthesis to focus on developing customized strategies for handling non-convex bilinear terms and of non-convexity. This will also help in overcoming the huge computational expense in solving real case industrial problems. It is also noteworthy that development of more meaningful optimization based formulations which are robust to handle wide range of problems and multiobjective problems is another way to handle water network synthesis problems. Application of robust optimization techniques and chance-constrained programming to problems under uncertainty has gained increasing attention (You, et al., 2009). This is due to the fact that robust optimization seeks to determine an optimal solution with respect to the original objective function and also ensures that constraints are feasible for all realizations of the uncertain parameters at a specified probability level (Khor, et al., 2014). Chance-constrained programming does not guarantee feasibility for all uncertainty problems, even for nominal parameter values, except for some desirable probabilistic constraints (Grossmann & Guillen-Gosalbez, 2010). Although both methods differ in attaining feasibility, in practice chance-constrained programming can provide a suitable mathematical framework to reformulate probabilistic constraints into a deterministic equivalent form (Khor, et al., 2014). Nonetheless both methods have an added advantage of requiring low computational recourse. It is also important to extend water network synthesis problems for materials and energy recovery in addition to water minimization. This kind of approach will not only minimize freshwater usage, it will also avoid violation of sustainability-related constraints pertaining to use of materials and energy (Sutton, et al., 2001).

6.8 Conclusion

Mathematical programming is characteristically theoretical and highly depends on empirical data available in literature. This chapter looks into methods that can be used to improve the solution procedure of mathematical models with similar structure like that encountered in this work. Variables and equations that are critical to obtaining a solution to models with less computational time are discussed. Highlighted also are shortcomings of the proposed model and algorithms that can be implemented to achieve faster solutions with a water network superstructure framework.

6.9 References

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CHAPTER 7

CONCLUSION

This work has addressed the synthesis of a multi-membrane regeneration water network by proposing a MINLP optimisation model that incorporates detailed mechanistic models of an ED and RO units within a water network. The developed water network allows for direct reuse and recycle and regeneration reuse/recycle. The developed MINLP model is applied to two illustrative case studies and one industrial case study to demonstrate its applicability. The first case study involves effluent with single contaminant in a pulp and paper industry. The second case study is a multi-contaminant framework, as naturally effluent will contain multiple contaminants. The third case study considers power utility plant in South Africa involving a single contaminant. All case studies were solved in GAMS using the general purpose global optimization solver BARON which uses the branch-and-reduce algorithm to obtain a solution. The model was run using a 64 Bit operating system windows 7 professional HP desktop computer with Intel® Core (TM) i7 – 4770 processor 3.40 GHz and 8.00GB of RAM.

Three scenarios were considered for the single contaminant case study. The first scenario considered water network superstructure model without regeneration, the second scenario considered a water network model with a “black-box” regeneration model and the third scenario considered detailed model of the regeneration unit within a water network superstructure. The second and third scenarios considered fixed and variable removal ratio for the regeneration units respectively. This lead to 43.7% freshwater reduction, 50.9% decrease in wastewater generation and 46% savings in total water network cost for detailed model as compared to the base case scenario.

The second case study also considered three scenarios as in case study 1. However, only variable removal ratio was considered for the regeneration units for both the first (“black-box”) and second (detailed) scenarios. Savings of up to 11.6% freshwater intake, 15.3% reduction in wastewater generation as well as 57.3% regeneration and energy were achieved for the detailed model. The model was finally applied to an industrial case study involving a power utility plant in order to minimise freshwater consumption, wastewater production and cost of water network. Just like the previous illustrative examples, three scenarios are considered. This resulted in savings of up to 18.7% freshwater consumption, 82.4% wastewater reduction and up to 17% savings on total water network cost.

The results in this work demonstrate that integrating detailed models of regeneration units in a water network superstructure results in significant reduction in water consumption as well as wastewater reduction in the process industry. This, however, comes with an increased cost of regeneration as the detailed model considers the true cost representation of the regeneration units as well as the WNS compared to the “black-box” representation. The optimal design of the membrane regeneration units also aids by given investors accurate cost representation for minimal energy usage.

The results showed that setting the removal ratio as variable yields optimal configuration as compared to the fixed removal ratio. The model also showed that incorporating a detailed model of the regeneration unit into the overall model yields accurate expression of the regeneration cost as compared to the ‘black-box’ model. It also gives optimal operating variables of the regeneration units for minimal energy usage.

The complexity of the model results in high computational time. However, this cannot be deemed a serious limitation in the context of synthesis and design, since this particular problem is solved once prior to the detailed design. It is noteworthy that the proposed model can be extended to include multiple regenerators.