SUPERSTRUCTURE OPTIMISATION OF A WATER MINIMISATION NETWORK WITH AN EMBEDDED MULTICONTAMINANT ELECTRODIALYSIS MODEL

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A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering

Supervised by Professor Thokozani Majozi

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Declaration

I, Chiedza Demetria Maputsa Nezungai (Student number 390172) am a student registered for the degree of Master of Science in Chemical Engineering in the academic year 2016.

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- I confirm that the work submitted for assessment for the above course is my own unaided work except where I have explicitly indicated otherwise.
- I have followed the required conventions in referencing the thoughts and ideas of others.
- I understand that the University of the Witwatersrand may take disciplinary action against me if there is a belief that this is not my own unaided work or that I have failed to acknowledge the source of the ideas or words in my writing.

C.D.M Nezungai

Synopsis

The water-energy nexus considers the relationship between water and energy resources. Increases in environmental degradation and social pressures in recent years have necessitated the development of manufacturing processes that are conservative with respect to both these resources, while maintaining financial viability. This can be achieved by process integration (PI); a holistic approach to design which emphasises the unity of processes. Within the realm of PI, water network synthesis (WNS) explores avenues for reuse, recycle and regeneration of effluent in order to minimise freshwater consumption and wastewater production. When regeneration is required, membrane-based treatment processes may be employed. These processes are energy intensive and result in a trade-off between water and energy minimisation, thus creating an avenue for optimisation.

Previous work in WNS employed a black box approach to represent regenerators in water minimisation problems. However, this misrepresents the cost of regeneration and underestimates the energy requirements of a system. The aim of the research presented in this dissertation is to develop an integrated water regeneration network synthesis model to simultaneously minimise water and energy in a water network.

A novel MINLP model for the design of an electrodialysis (ED) unit that is capable of treating a binary mixture of simple salts was developed from first principles. This ED model was embedded into a water network superstructure optimisation model, where the objective was to minimise freshwater and energy consumption, wastewater productions, and associated costs. The model was applied to a pulp and paper case study, considering several scenarios. Global optimisation of the integrated water network and ED design model, with variable contaminant removal ratios, was found to yield the best results. A total of 38% savings in freshwater, 68% reduction in wastewater production and 55% overall cost reduction were observed when compared with the original design. This model also led to a 80% reduction in regeneration (energy) cost.

Publications

Below is a list of publications and conference presentations resulting from the work presented in this dissertation:

Journal Publications

Nezungai, C.D. & Majozi, T. 2016, 'Optimum synthesis of an electrodialysis framework with a Background Process I: A Novel Electrodialysis Model' *Chemical Engineering Science*, 147, 180-188.

Nezungai, C.D. & Majozi, T. 2016, 'Optimum synthesis of an electrodialysis framework with a Background Process II: Optimization and synthesis of a water network' *Chemical Engineering Science*, 147, 189–199.

Book Section

Nezungai, C.D. & Majozi, T. 2015, 'Superstructure Optimisation of a Water Minimisation Network with an Embedded Multi-Contaminant Electrodialysis Model', in: Krist V. Gernaey, J.K.H. and R.G. (Ed.), *Computer Aided Chemical Engineering*, Elsevier, pp. 845–850.

Conference Presentations

Nezungai, C.D. & Majozi, T. 2015, 'Optimisation of Integrated Water and Membrane Network Systems using Process Integration' paper presented at the *South African Institute of Chemical Engineers Conference*, 31 July-3 August, Durban

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Nezungai, C.D. & Majozi, T. 2015, 'Superstructure optimisation of a water minimization network with an embedded multi-contaminant electrodialysis model', paper presented at the *25th European Symposium on Computer Aided Process Engineering and Process Systems Engineering Conference*, 31 May -4 June, Copenhagen

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"A bend in the road is not the end of the road unless you refuse to take the turn."
Unknown

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List of Acronyms

AEM	Anion Exchange Membrane
BARON	Branch and Reduce Optimization Navigator
BOD	Biochemical Oxygen Demand
CEM	Cation Exchange Membrane
COD	Chemical Oxygen Demand
CWSS	Complete Water System Synthesis
ED	Electrodialysis
EDBM	Electrodialysis with Bipolar Membranes
EDI	Elecrodeionization
ETS	Effluent Treatment System
FO	Forward Osmosis
GAMS	General Algebraic Modelling System
GDP	General Disjunctive Programming
HEN	Heat Exchange Network
IP	Integer Programming
LP	Linear Programming
MD	Membrane Distillation
MDG	Millennium Development Goals
MEN	Mass Exchange Network
MF	Microfiltration
MILP	Mixed Integer Linear Programming
MINLP	Mixed Integer Nonlinear Programming
MIP	Mixed Integer Programming
NF	Nanofiltration
NLP	Nonlinear Programming
PI	Process Integration
RMINLP	Relaxed Mixed Integer Nonlinear Programming
RO	Reverse Osmosis
SS	Suspended Solids

TDS	Total Dissolved Salts
TWNS	Total Water Network Synthesis
UF	Ultrafiltration
WN	Water Network
WNS	Water Network Synthesis
WPA	Water Pinch Analysis
WRNS	Water Regeneration Network Synthesis
WUN	Water Using Network

1

INTRODUCTION

1.1 Background

In 2000, The United Nations stipulated eight global goals aimed at improving the lives of people in developing nations such as South Africa. These are known as the Millennium Development Goals (MDG).Water conservation and the reduction of greenhouse gas emissions are critical to the attainment of the 7th MDG, which is “to ensure environmental sustainability” (United Nations, 2015).

Water scarcity is an environmental phenomenon wherein the amount of water available to a given community is insufficient to cater for the needs of that community. As depicted in Figure 1.1, most countries in Sub-Saharan Africa experience either physical or economic water scarcity. Physical water scarcity occurs in dry areas or when the demand for water exceeds the amount of water that can be produced in a particular region. Economic water scarcity on the other hand, occurs when available resources are unequally distributed and water access is limited to only part of a population; this is often due to political imbalance or ethical conflict (United Nations, 2012). According to the South Africa Yearbook of 2013/14, South Africa is the 30th most water scarce country in the world (Government Communications and Information System, 2014).

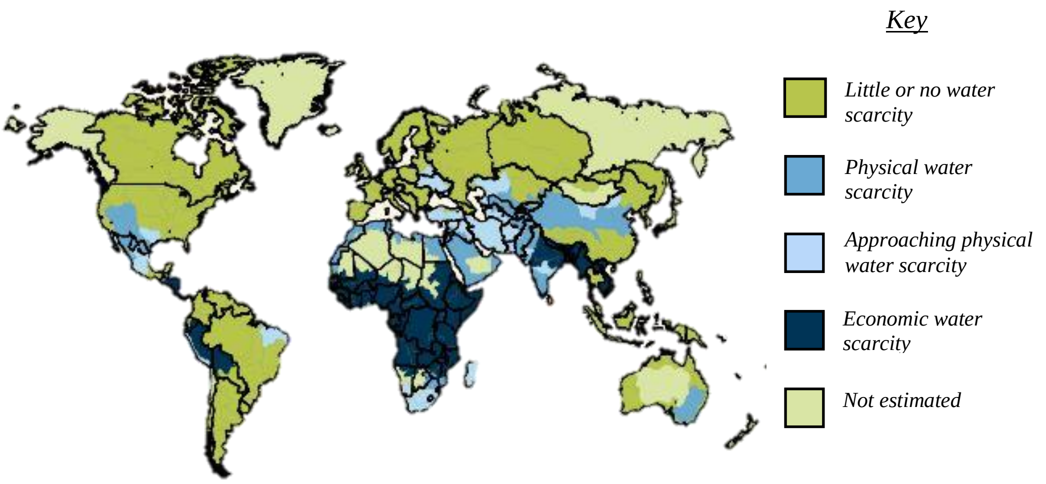

Figure 1.1: Global economic and physical water scarcity (United Nations, 2012)

In response to water scarcity and the desire for sustainable process engineering, many policy makers, companies and individuals have taken initiatives to minimise water consumption. Industrial processes make up 17% of water consumption in South Africa, and as a result, significant responsibility for conservation lies with process industries (Council for Scientific and Industrial Research, 2010)

Electricity is a fundamental utility in all process industries. However, in addition to being expensive, generation of electricity is often achieved by fossil fuel combustion, which results in the emission of greenhouse gases such as carbon dioxide and methane. This has led to the increase in the surface temperature of the earth over time, a phenomenon known as global warming. Global warming is responsible, in part, for several challenges faced by the earth in recent years, including shifting weather patterns, a loss of biodiversity and a rise in sea levels (Intergovernmental Panel on Climate Change, 2014).

This global crisis has prompted process industries to take steps to minimise the amount of emissions in manufacturing. Emissions reduction is of particular concern in South Africa as it is one of the 20 largest global emitters of greenhouse gases (Emission Database for Global Atmospheric Research, 2014). This is owed to the fact that 90% of the energy produced locally is fossil fuel dependent, i.e. coal, natural gas and oil. The remaining 10% is derived from nuclear and renewable energy resources (Government Communications and Information System, 2014b).

It is necessary to acknowledge the interdependence of water and energy resources. Water is used in the production of energy, either directly via hydroelectric and geothermal means or indirectly as steam to turn turbines. Conversely, energy is used in the extraction, distribution and treatment of water. This relationship between water and energy is known as the *water-energy nexus* (Desai, 2013). Because of this nexus, it is important to address water conservation and energy minimisation simultaneously and develop processes that are efficient in both regards.

This can be achieved by the use of process integration (PI), a holistic approach to process design and operation that emphasises the interaction of all components in a system. Process integration involves the synthesis, analysis and optimisation of processes (El-Halwagi, 1997). In the context of water conservation, PI explores avenues for reusing or recycling water within a given processing plant. Recycling is the channelling of reusable water to the process in which it was generated, while reuse is the use of reusable water in other processes. Often, before water can be reused it must be regenerated, i.e. contaminants must be partially or completely removed (Wang and Smith, 1994). Water regeneration processes, such as reverse osmosis, electrodialysis and nanofiltration, are generally energy intensive. As a result, industries are faced with a trade-off between minimising water consumption and minimising energy consumption and cost of regeneration.

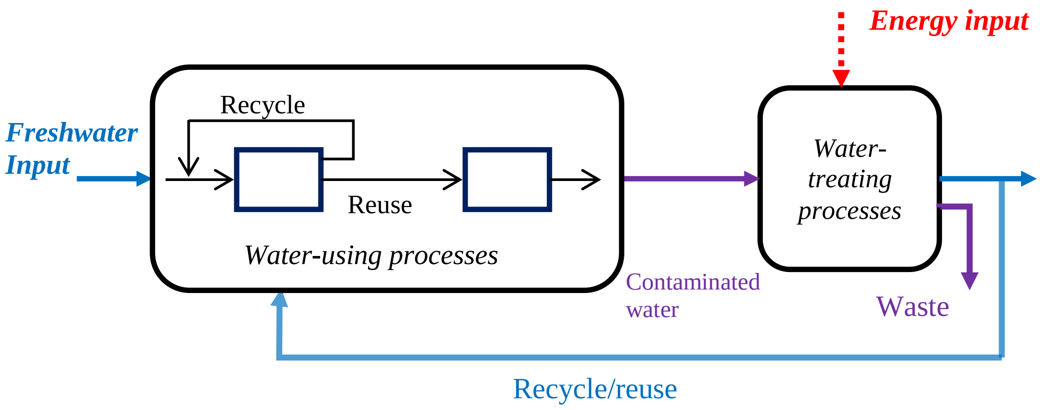

Figure 1.2: Schematic representation of the interaction between water using processes and water treating processes in a water network

By considering the interconnections between *water-using processes*, that consume and produce water, and *water treating processes* in a plant, a water network can be synthesised, as shown in Figure 1.2. Common approaches to water network synthesis (WNS) include pinch analysis and the use of superstructure-based mathematical models. A superstructure captures all feasible possibilities of reuse, recycling and regeneration. Optimisation methods are then used to select the optimum configuration. To date, most work in this field has taken a generalised or *black box* approach in representing the regeneration processes, due to their computational complexity. In black box modelling, the treatment units are simplified and described using only a single performance expression such as the removal ratio (Chew et al., 2008; Khor et al., 2012a). However, this results in misrepresentation of the unit design requirements and cost of treatment and introduces the possibility of understating the energy consumption. In order to accurately synthesise and optimise a water network, the design of the regeneration unit must be accounted for completely (Khor et al., 2011).

In this dissertation, the regeneration process under consideration is electrodialysis (ED). This process is characterised by the electromigration of ions across a series of selectively permeable membranes under the influence of an applied direct electric current (DC). The optimal design of an electrodialysis unit involves the determination of physical characteristics as well as operating conditions required to minimise the energy consumption. Many existing ED optimisation models have been developed considering only single contaminant systems (Lee et al., 2002; Tsiakis and Papageorgiou, 2005). Electrodialysis is most commonly used for the desalination of seawater, which consists mainly of sodium chloride. In such cases, single contaminant representation is adequate. However, most industrial processes contain several contaminants; it is therefore necessary to develop a model that caters for multicontaminant, multivalent effluent streams (Brauns et al., 2009).

Simultaneous water and energy minimisation in processing plants has previously focused on the integration of water allocation networks and heat exchanger networks (Zhou et al., 2012a, 2012b). The research presented in this dissertation focuses on the minimisation of energy specifically within the water network, i.e. energy associated with regeneration. This is achieved by the inclusion of a detailed electrodialysis design within the water minimisation problem. In addition, the model attempts to minimise the capital costs associated with retrofitting a regeneration unit to an existing system, and the total wastewater produced.

1.2 Scope

This work involves the development of a novel multicontaminant electrodialysis design model. Electrodialysis design can be conducted based on the rate of diffusion of ions across the membranes, the convection of fluids along the channels or limiting current density of the unit. In this work, the limiting current density is used as the basis of design. Previous similar models have considered only single contaminant feed; in this work, these models are extended to cater for multicontaminant feeds. The electrodialysis model is then considered for partial purification of contaminated water within a water network synthesis and optimisation problem. Mathematical optimisation techniques are used for the development of the water network, taking the fixed flowrate approach for the representation of water-using processes. The work aims to emphasise the limitations of the widely used black box approach while highlighting importance of simultaneous energy and water minimisation in water network optimisation. This will be done by applying the developed model to a case study and comparing it to various modelling scenarios, including the black box approach.

1.3 Objectives

The research presented in this dissertation pursues the following objectives:

(i) To develop a detailed, standalone optimisation model of a multicontaminant electrodialysis unit to minimise operation and capital costs. In so doing, it is desired to obtain the optimum operating and design conditions of the electrodialysis unit including current, voltage length, area and the number of cell pairs.

(ii) To develop a complete water network superstructure which is the basis for a mathematical optimisation approach for water minimisation.

(iii) To integrate the electrodialysis standalone model with the water network superstructure in order to develop an approach for simultaneous water and energy minimisation in a water network. The overall objective function, expressed as a cost function, minimises the amount of freshwater consumed, wastewater produced, the energy consumed in the regeneration unit and the piping costs (both capital and operational), associated with retrofitting the new plant design.

1.4 Dissertation Structure

This dissertation is presented in six chapters, as follows:
Chapter 1 – Introduction. The current chapter provides the background of the problem, and illustrates the purpose of the investigation at hand. The scope and objectives of the study are also given.

Chapter 2 – Literature review. A review of relevant literature is given, providing the basis upon which the models are developed. This includes key milestones in the field of water network synthesis and electrodialysis design, as well as the mathematical optimisation theories and techniques applied in the model development.

Chapter 3 – Model development. A detailed derivation of an electrodialysis model is presented, from first principles. Two alternative models, based on different assumptions of solution conductivity, are given. Secondly, the development of a superstructure-based water network model is described. This water network includes the detailed electrodialysis model.

Chapter 4 – Model application. In this chapter, the two electrodialysis models are compared and evaluated by applying them to a pulp and paper case study. Secondly, the water network model is applied to a separate case study. Three scenarios are considered to compare the effects of process integration under different conditions.

Chapter 5 – Limitations and Recommendations. Some of the challenges faced in the model development and application are addressed in this chapter. Also included are model limitations and suggestions for improvements to the model in future.

Chapter 6 – Conclusion. The final chapter summarises the model developed and evaluates the success of this model in solving the problem presented.

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2

LITERATURE REVIEW

2.1 Introduction

This chapter is a review of the literature that is used to provide the basis for the research conducted. First, a brief outline of the principles of mathematical optimisation is given. This is followed by a broad and comprehensive review of water network synthesis and optimisation modelling. This includes the characteristics of water networks, different modelling methods, water minimisation approaches and techniques used in mathematical optimisation of water networks. An introduction to membrane systems for wastewater treatment is given, followed by a detailed description of the process of electrodialysis and associated modelling and optimisation methods. To conclude, key works in WNS synthesis with partial regeneration are considered.

2.2 Mathematical Modelling and Optimisation

A mathematical model is defined by Eykhoff (1974) as “a representation of the essential aspects of an existing system (or system to be constructed) which represents knowledge of that system in a usable form”. It is made up of mathematical relationships such as equations, inequalities and logical expressions that describe a physical situation or system. Mathematical modelling is beneficial as it reveals relationships within a system that are not immediately apparent. It also allows the analysis of these relationships while avoiding experimentation (Williams, 1997). This is important especially when the consequences of experimentation may be undesirable or expensive, as is often the case in processing plants. For example, it may not be practical to manually explore the effect of temperature on processes in a petroleum refinery, as it may result in damaged equipment, wasted raw materials or contaminated products.

Optimisation is a field of applied mathematics that involves finding the extremal value of a function in the domain of definition, subject to constraints on variable values (Liberti, 2008). It can be achieved by the use of a mathematical programming model where there is at least one expression to be minimised or maximised. This expression is known as the *objective function* and it is subjected to a combination of equality and inequality constraints. In an event where the objective function and all the equality and inequality constraints are linear expressions, the model is a *Linear Programming* model (LP). If any one of the constraints or objective functions are nonlinear, it is known as *Nonlinear Programming* (NLP) model. Nonlinearities make a model more complex to solve. Such problems can be linearized to make them easier to solve, but this may come at the expense of solution accuracy. Natural phenomena are often described by continuous variables and expressions. However, in some cases it is necessary to specify that variables are whole numbers, i.e. *integers*. This unique case is known as *Integer Programming* (IP) or more commonly *Mixed Integer Programming* (MIP), when the model involves a combination of discrete and continuous variables. Depending on the nature of the constraints, MIPs are further divided into *Mixed Integer Linear Programming* (MILP) and *Mixed Integer Nonlinear Programming* (MINLP) problems (Williams, 1997).

The most generalised expression of an optimisation problem is given for an MINLP according to Equations (2.1)-(2.4) (Liberti, 2008). Equation (2.1) represents the objective function to be minimised and Equation (2.2) represents both the equality and inequality constraints. Equation (2.3) represents a unique type of inequality constraint known as the *variable bounds*, where the value of a variable, x, must be greater than the lower bound, x^L, and less than the upper bound x^U. Equation (2.4) represents the variables, x_i, that are only allowed to take integer values.

Minimise $\quad f(x)$ $\quad$ *(2.1)*

Subject to $\quad g(x)\{\leq,=,\geq\}b$ $\quad$ *(2.2)*

$$x^L \leq x \leq x^U \quad (2.3)$$

$$x_i \in \mathbb{Z} \qquad \forall i \in Z \quad (2.4)$$

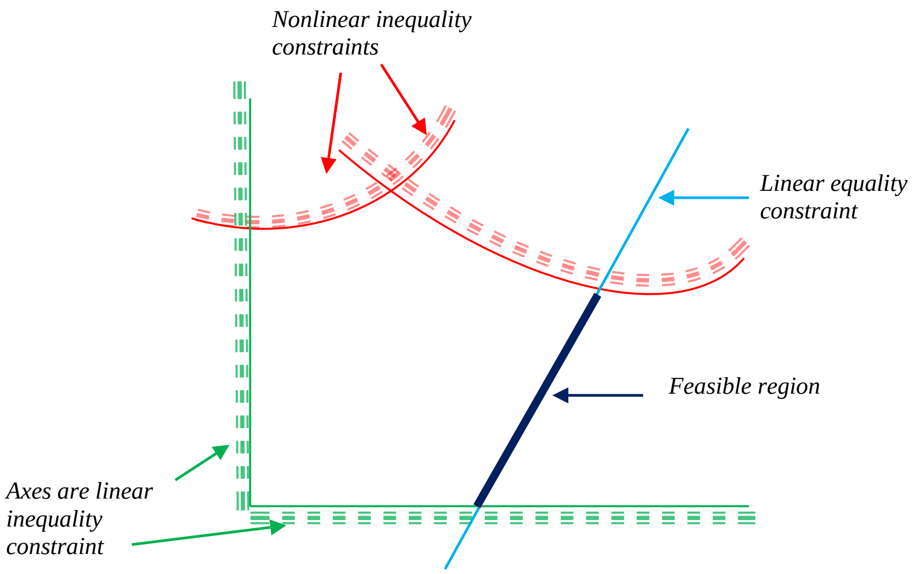


Figure 2.1: Feasible region for an optimisation problem involving two independent variables (Edgar and Himmelblau, 1988)

A *feasible solution* is a set of variables that satisfy the constraints of an optimisation problem, while the *feasible region* represents all the feasible solutions in the given problem. An *optimal solution* is a feasible solution that provides the best value of the objective function (Edgar and Himmelblau, 1988). Figure 2.1 depicts the relationship between the feasible region and the different types of constraints. The dashed lines of the inequality constraints represent the infeasible region.

An important classification of functions in optimisation is whether a model is convex or concave. Convexity can be described, for a function, *f(x)*, according to Equation (2.5), where $\theta \in [0,1]$ (Edgar and Himmelblau, 1988).

$$f[\theta x_a + (1-\theta)x_b] \leq \theta f(x_a) + (1-\theta) f(x_b) \qquad (2.5)$$

Similarly, a function, *f(x)*, is concave if

$$f[\theta x_a + (1-\theta)x_b] \geq \theta f(x_a) + (1-\theta) f(x_b) \qquad (2.6)$$

These expressions are depicted graphically in Figure 2.2. A straight line is drawn between two points on a curve *f(x)*. If the points on the curve are less than or equal to the points on the straight line, the function is described as *convex* (Figure 2.2a), conversely if the points on the curve are greater than or equal to the points on the straight line, the function is *concave* (Figure 2.2b)(Edgar and Himmelblau, 1988).

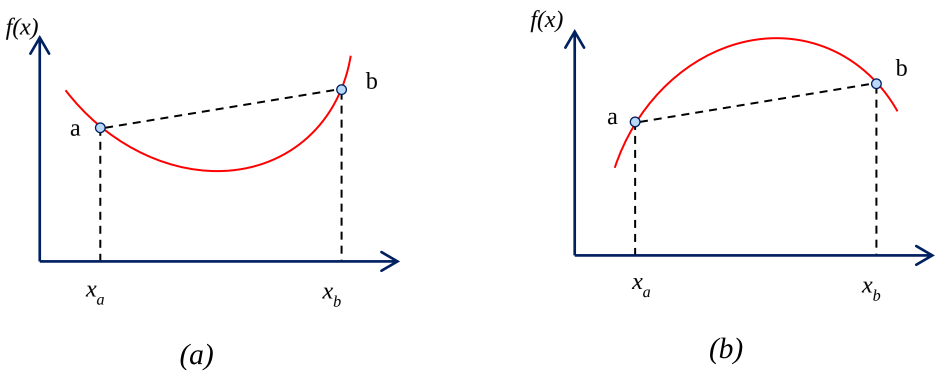


Figure 2.2: Graphical comparison of (a) convex and (b) concave functions

Strictly convex or concave problems provide a single optimum solution whereas a nonconvex function may have multiple optimum solutions (*local optima*). It is difficult to guarantee whether the whether a solution provided is actually the *global optimum*, which is the best of all local optima. This concept is illustrated in Figure 2.3.

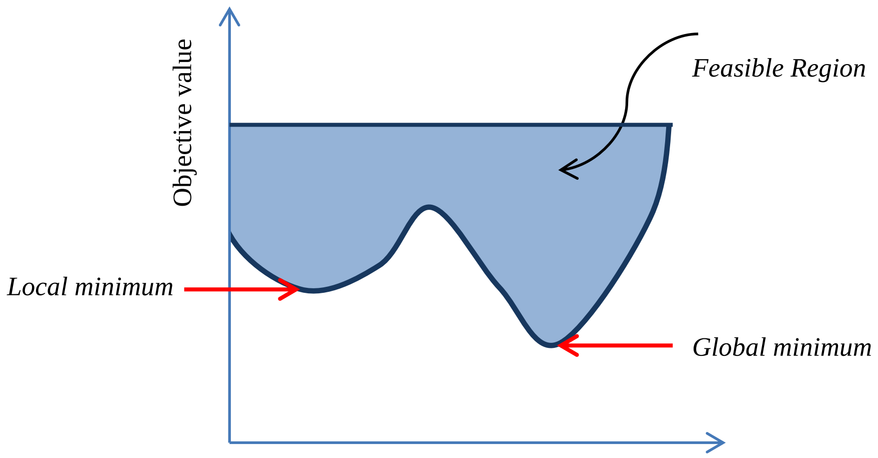


Figure 2.3: Illustration of a local and global minimum of a nonconvex function

When mathematical optimisation is applied to chemical engineering situations the problems are most often framed as Mixed Integer Nonlinear Programming model (MINLP), as this encompasses the continuous variables as well as binary variables which are often necessary for the structure of a problem. This framework has been applied to process synthesis problems such as energy recovery networks, water network synthesis, separation systems, reactor network, process operation problems such as scheduling and other design and synthesis problems. The complexities in solving these problems arise from the existence of integer variables, nonlinearities and non-convexities (Adjiman et al., 1997).

2.3 Water Network Synthesis

Water minimisation, in process optimisation, is the reduction of freshwater consumed on a particular processing plant, as well as a reduction in the amount of wastewater produced. This is achieved by the development of water networks (WN), which can either be designed for new plants or retrofitted to existing plants. A water network is a collection of *water using processes,* that either require or produce water, and operations that purify wastewater, *regeneration processes*. Other elements of a WN may include freshwater sources, wastewater disposal sites, mixers, splitters and sometimes storage tanks (Jeżowski, 2010)

2.3.1 Characteristics of Water Networks

Water using processes can be further classified as mass transfer or non-mass transfer processes. Mass transfer operations, also known as quality controlled or fixed load operations, are characterised by the mass load of contaminants that should be carried by the water; these include solvent extraction, absorption and equipment washing. Non-mass transfer processes are also known as quantity controlled or fixed flowrate operations (Jeżowski, 2010). These are further divided into water sources and water sinks. A w*ater sink* is a process that consumes water; its demand is satisfied by a mixture of freshwater, reuse/recycle water from the sources and regenerator products. A w*ater source* produces water that may be used in the sinks, the regenerator or discharged as waste (Tan et al., 2009).

Water networks consisting only of sources and sinks are known as water-using networks (WUN). The class of water network synthesis problems that allows for partial treatment of effluent is known as water regeneration network synthesis (WRNS). When the system is extended to include a centralised end-of-use effluent treatment system (ETS) it is known as total water network synthesis (TWNS). The combination of TWNS and pretreatment networks results in a complete water system synthesis (CWSS)(Khor et al., 2014).

2.3.2 *Water Minimisation Approaches*

Water consumption in process plants can be altered by affecting the process conditions, such as temperatures, pressures and feed conditions. However, excluding the possibility of affecting the actual process under consideration there are four water recovery schemes adopted in process integration (Wang and Smith, 1994). These are illustrated in Figure 2.4.

Direct reuse. Effluent produced by one source is then reused in other operations, provided that the level of contamination does not interfere with the process. This case is shown in Figure 2.4a.

Direct recycle. A subset of water reuse, effluent is channelled back into the process in which it was produced, as depicted in Figure 2.4b. In both reuse and recycle, effluent can be blended with water from other operations or freshwater before it is reused or recycled.

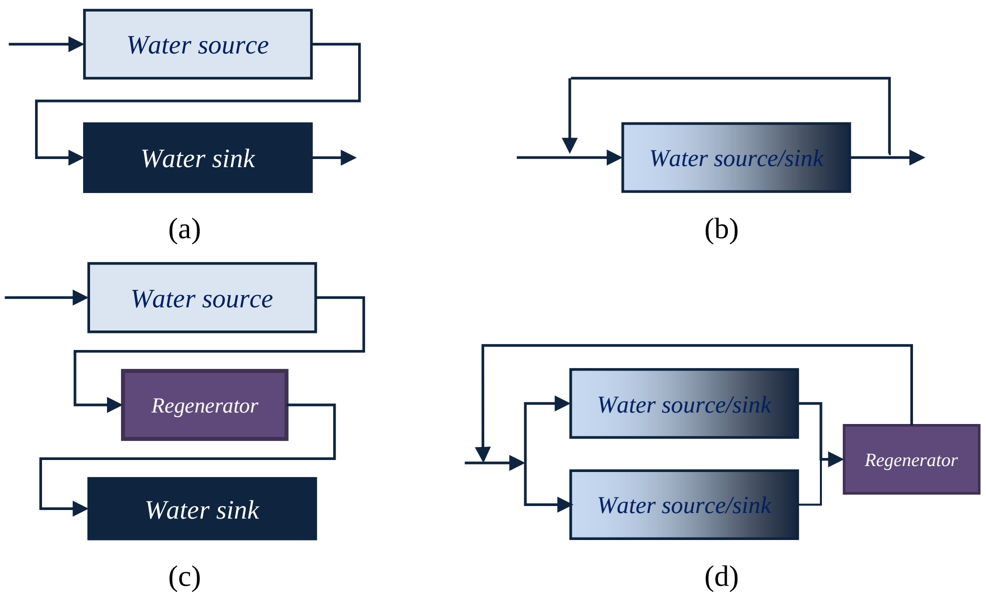


Figure 2.4:Schematic diagrams illustrating water recovery schemes

Regeneration reuse. As shown in Figure 2.4c, water from a source can be partially treated to remove contaminants, i.e. water is regenerated, to make it amenable for reuse in other sinks.

Regeneration recycle. Effluent is partially treated to remove contaminants that may have built up, and then recycled into the same operation. This is depicted in Figure 2.4d.

The combination of the above four cases results in water regeneration network synthesis (WRNS). Partial purification can be performed by the use of membranes, chemical additives, and steam stripping, among other processes (Cheremisinoff, 2002). When synthesizing water networks, for optimal operation, a combination of all schemes must be allowed. While regeneration reduces water consumption, this may come at the expense of energy and a high capital investment. Kim (2012) explored the cost implications of the different water minimisation scenarios; the comparison is shown in Figure 2.5.

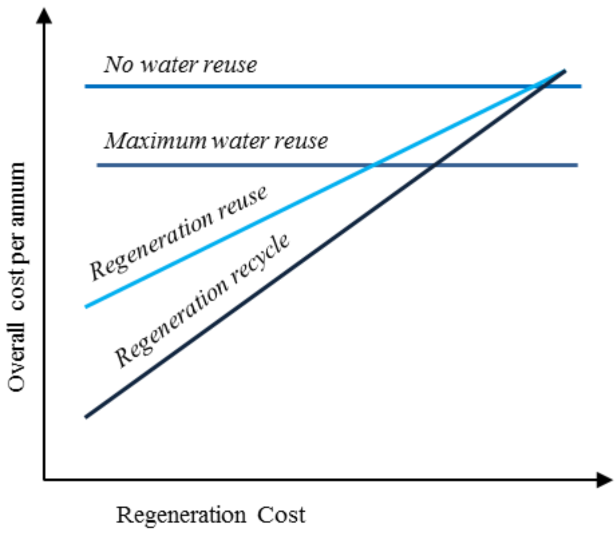


Figure 2.5: Relationship between regeneration cost and overall water network cost for different water recovery schemes (Kim, 2012)

For a low regeneration cost, it is profitable to consider regeneration recycle and regeneration reuse. However, at high regeneration costs, direct reuse becomes more profitable. This emphasizes the importance of accurately considering regeneration costs when developing a water network optimisation framework.

2.3.3 Water Network Synthesis and Optimisation Methods

There are two main approaches commonly employed when addressing water network problems. These are known as insights based techniques and mathematical model based optimisation techniques.

Insights Based Methods

In water network optimisation, the most common insights based method is *water pinch analysis* (WPA), which is a graphical technique. The method of pinch technology was initially developed for heat integration in heat exchanger networks (HENs) by Linnhoff and Hindmarsh (1983). They developed a method for the minimisation of energy and utilities in a heat exchanger network, while simultaneously reducing the number of required heat exchange units. This was achieved by identifying and exploiting thermodynamic bottlenecks, known as pinch points in the systems. The optimal HEN was then developed based on the location of the pinch points, rather than a mere comparison of the available and required energy in the hot and cold streams in the network. As a result, it was possible to achieve the highest degree of energy recovery at a minimum capital expense. The same concept was later applied to the synthesis of mass exchange networks (MENs) (El-Halwagi and Manousiouthakis, 1989). In this case, the technique was used to improve the configuration of MENs to maximise the amount of a species that can be transferred between rich and lean process streams of the network.

The pinch technique was applied to a water minimisation case, a subset of MENs, by Wang and Smith (1994a). In this work, the concept of the limiting water profile and minimum driving force were introduced as a means to determine the optimal freshwater flowrates required in a system. This concept can be represented in the composite curve, Figure 2.6, that shows the relationship between concentration, C, and impurity load, Δm, for a process stream (rich stream) and a wash water stream (water profile). The limiting water profile depicts the case when the inlet and outlet concentrations of the wash stream are set to their maximum values. This corresponds with the minimum wash water flowrate, and subsequently, minimum freshwater consumption, owing to maximum reuse and recycle.

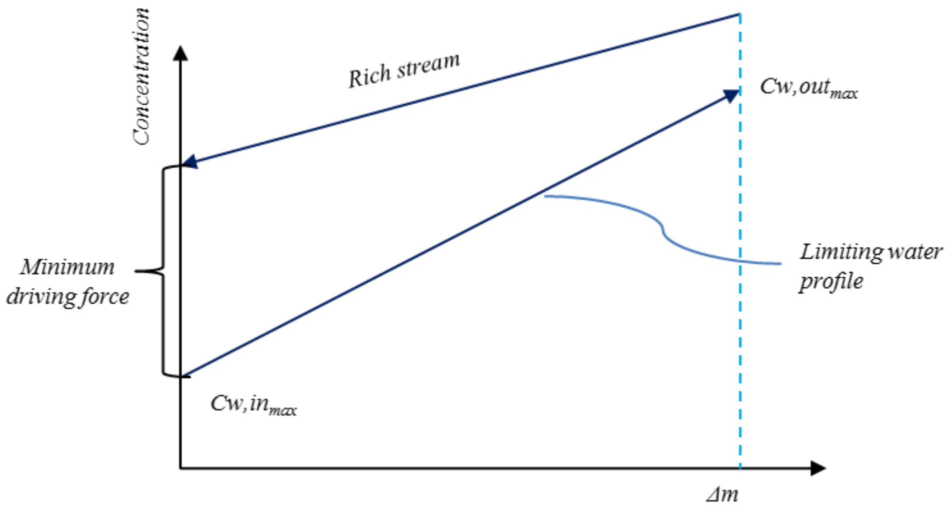


Figure 2.6: Limiting composite curve for a washing operation indicating the limiting water profile (Wang and Smith, 1994a)

When a process, is operated under limiting water profile conditions, maximum water recovery potential is achieved. By targeting maximum reuse, Wang and Smith (1994a) were able to minimise freshwater consumption for an entire water network. Wang and Smith (1994b) extended this formulation to include multiple contaminants, by designing a subnetwork for each contaminant then merging them into a consolidated design.

When considering a network of water using operations, a combined composite curve can be drawn in series, as shown in Figure 2.7 for four separate streams. To target minimum water flowrate a water supply line is drawn. The minimum target water flowrate is represented by the steepest possible water supply line that just touches the limiting composite curve. The point of intersection between the two curves is known as the *pinch point*. This concept is demonstrated using an example given by Smith (2005). In this example, the minimum water flowrate is 90t/h and the flowrate required above the pinch is 45.7 t/h.

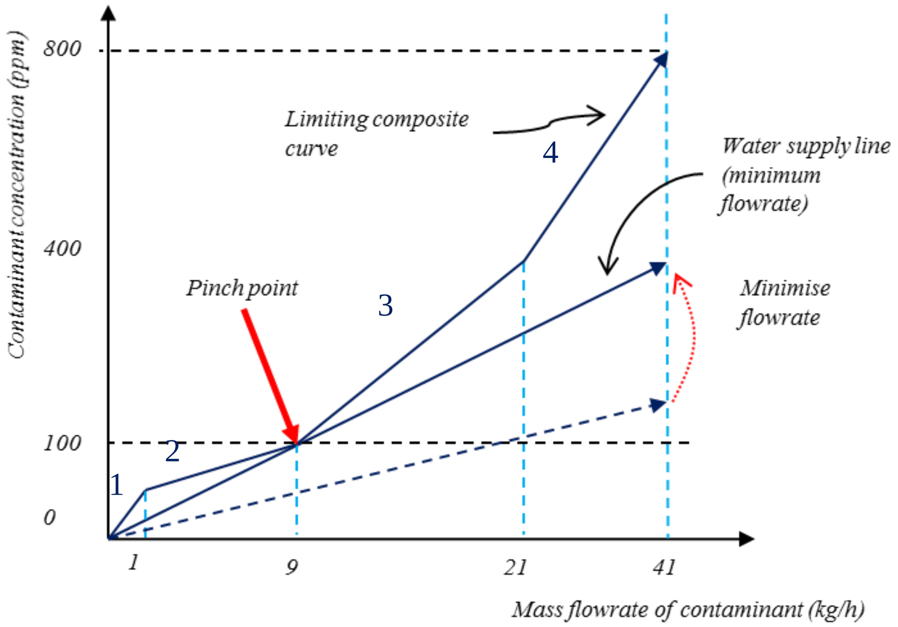


Figure 2.7: Targeting minimum water flowrate for a single contaminant (Smith, 2005)

Having determined the minimum target flowrate, it is possible to then design the water network in order to achieve that target. In the above example, two regions are identified; above the pinch and below the pinch. Kuo and Smith (1998a) define a four-step design procedure based on setting up hypothetical *water mains* which act as sources or sinks depending on their position.

Step 1: Set up the design grid. A design grid is developed by setting up three water mains corresponding to the freshwater concentration (source), pinch concentration (source and sink) and maximum concentration (sink). The design grid represents the flowrate of water required by each main and wastewater generated by each main. This is illustrated in Figure 2.8, based on the same example as above.

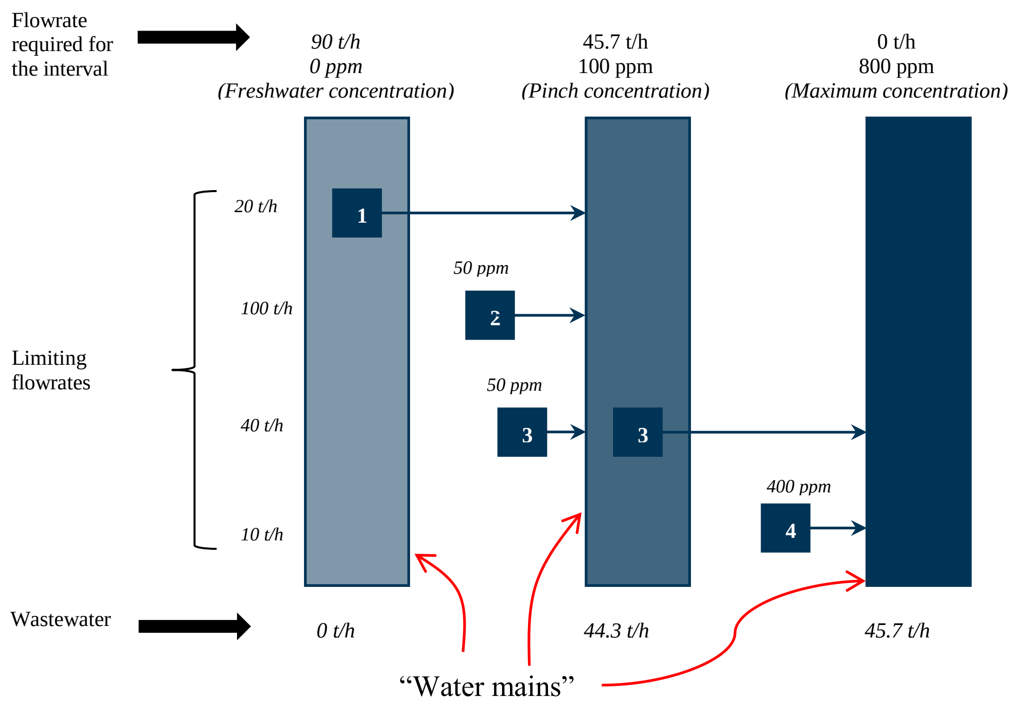


Figure 2.8: Design grid for the water network (Smith, 2005)

Step 2: Connect operations with water mains. The streams representing the individual operations are superimposed on the water mains to satisfy the requirements of each operation. Four operations are shown in Figure 2.8.

Step 3: Merge operations crossing boundaries. In cases where operations cross the water main, the grid represents it as two separate operations. This implies a change in flowrate in the middle of the process, which is impractical. The necessary streams are merged before the process, resulting in a single operation. Operation 3 in Figure 2.8 crosses the intermediate water main.

Step 4: Remove the intermediate water mains. The intermediate main, which acts as a source and sink, can be removed once the operations are paired up correctly. Sources can connect with sinks directly as long as the supplying and required flowrates are matched and process constraints, such as piping layout, are considered. The resultant design grid, after removing the intermediate main is shown in Figure 2.9. The corresponding flowsheet is depicted in Figure 2.10.

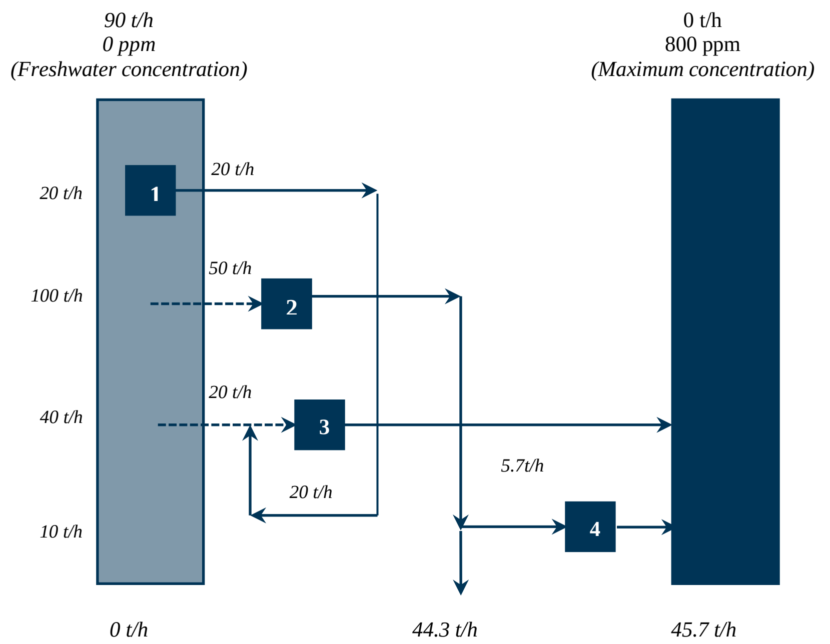


Figure 2.9: Final design grid of the water network without the intermediate water main (Smith, 2005)

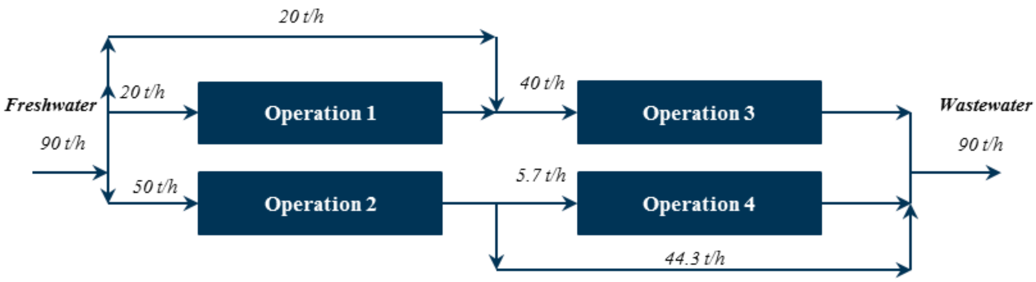


Figure 2.10: Resultant flowsheet of the water network (Smith, 2005)

For more complex problems, WPA makes use of certain heuristics to simplify the problem in order to be able to solve it graphically. For example;

- Minimise the flowrate of a sink to reduce the overall fresh resource intake, and
- Maximise the inlet concentration of a sink to maximise material recovery (Foo, 2012)

These simplifications have the potential of compromising the accuracy of the solution obtained or resulting in suboptimal water network designs. WPA has since been extended to include effluent treatment systems (Kuo and Smith, 1998b). It has also been modified to incorporate non-mass transfer processes such as reactors and cooling towers, thus improving the applicability of the technique (Hallale, 2002). The main advantage of WPA is the ability to gain reasonable insights into the design of a plant at low computational expense. Major developments in WPA are explored in the works of Foo (2009), Jeżowski (2010) and Khezri et al. (2010).

Mathematical Optimisation

The mathematical programming approach of water networks is based on the optimisation of a network superstructure. The superstructure of a water network is a description of all possible feasible connections between water using processes and water treating processes. The optimal solution is a subset of the superstructure and is identified by the use of optimisation methods. The technique was initially developed in the late seventies, where Takama et al. (1980a) proposed the combination of all possible water allocation and treatments options in a petroleum case study into one integrated system. The preferred option was selected by identifying the variables that resulted in the minimum cost, subject to material balances and interrelations among water-using and wastewater-treating units. The mathematical model presented was an NLP and was solved using an algorithm known as the Complex Method. The authors stated that this method was inefficient for application to large problems. In subsequent works, a modified solution procedure was proposed. This method involved the iterative application of linear programming to linearize the problem. To reduce the complexity of the problem, heuristics, based on practical and economic reasoning were applied to remove unnecessary features of the water network. For example, recycling within a water treatment unit was forbidden; and freshwater streams were prohibited from directly entering treatment units (Takama et al., 1980b, 1981,).

After several years, Doyle and Smith (1997) conducted a study that combined the works of Wang and Smith (1994a, 1994b) and Takama et al., (1981, 1980a, 1980b). The authors used graphical methods to attain physical insights into the parts of the system that require most attention, i.e. pinch points. The mathematical approach involved iterative solutions of both linear and nonlinear models, taking into account the insights provided by the graphical techniques. This work also enabled the simultaneous modelling of multicontaminant systems. Similarly, Hallale (2002) presented a method that combined both WPA and mathematical methods. A graphical technique was used to identify the pinch point. Using the insights gained from the composite curves, mathematical models were used to design the network.

Mathematical optimisation provides the benefit of being able to handle complex systems, e.g. multiple contaminants and water regeneration network synthesis. However, due to the fact that WNS problems are often nonlinear, the computational expense is often very high. Several advancements have since been made in the field, and these have been discussed at length in reviews by (Bagajewicz, 2000; Jeżowski, 2010; Khor et al., 2014). Chapter 2.3.4 highlights some of the challenges and advancements in mathematical modelling of WNS.

2.3.4 *Mathematical Methods in Water Network Optimisation*

Mathematical models for WNS are based on the pooling problem, which was initially developed to describe the flow and mixing of products in a petroleum plant. The pooling problem is stated as follows:

Given a list of suppliers (inputs) with raw materials containing known specifications, what is the cheapest way of mixing these materials in intermediate tanks (pools) so as to meet the demand and specifications at multiple final blends (outputs)? (Gupte et al., 2013).

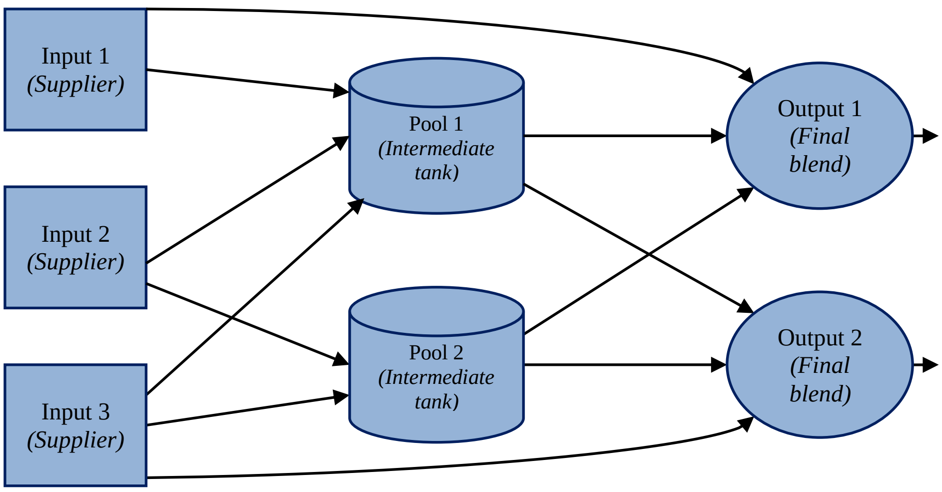


Figure 2.11: Sample pooling problem for a refinery (Gupte et al., 2013)

Figure 2.11 shows the interaction between three nodes of a pooling problem: inputs, pools and outputs. The pools serve as mixing and splitting junctions that allow the combination of raw materials and subsequent distribution of products to form the final blends.

This concept is adopted in the development of superstructures for WNS, where the inputs are water sources, outputs are water sinks and pools are mixers, splitters and water treatments units (Meyer and Floudas, 2006; Misener and Floudas, 2010). In the generalised pooling problem presented by Meyer and Floudas (2006) the network topology is presented as a decision variable. For example, the existence of a particular stream is determined by the introduction of a binary variable which is activated, i.e. equal to one, when the stream exists, and deactivated when the optimal topology excludes the stream.

The WNS optimisation problem is most commonly formulated as a mixed integer nonlinear programming problem (MINLP), following the general structure defined in Chapter 2.2. The mixed integer variables are due to the combination of continuous variables and binary variables introduced to activate or deactivate streams and treatment units. The nonlinearity is generally due to bilinear terms that occur in the contaminant balances when multiple streams mix in pooling nodes, when linear blending is assumed. Linear blending implies that the total load of a contaminant at a node is the sum of the product of the contaminant concentration and the total flow of each input to the node (Gupte et al., 2013). The activation and deactivation of streams also introduce bilinear terms to the model.

Fixed Load and Fixed Flowrate Approaches

In many of the insights-based works that dominated the field of WNS in early years, water networks were based on the fixed load or fixed outlet concentration. WPA is an extension of mass exchange networks, and so the processes considered in WNS were mainly mass transfer processes, such as washing operations, solvent extraction and gas absorption. This approach was then adopted into the early mathematical optimisation formulations between the years 1994-2000 (Foo, 2009). The fixed load approach considers counter-current exchange of a fixed amount of contaminant, L_p, between a process and a water stream, as depicted in Figure 2.12. Emphasis in mass transfer processes is on maximising load removal rather than minimising water flowrate. The water flowrate is assumed constant and water gains or losses are negligible.

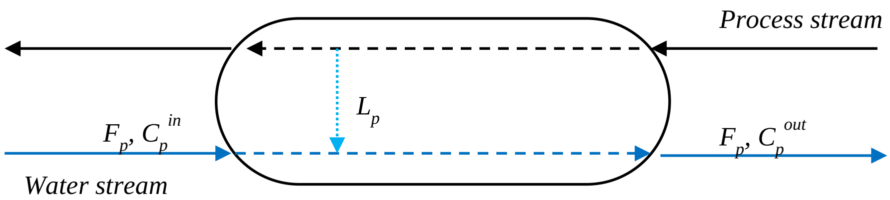


Figure 2.12: Water scheme of a fixed load mass transfer processes (Poplewski et al., 2011)

It is possible, and often more convenient, to separate the water using process into two units, a source and a sink. This separation results in what is known as the fixed flowrate approach; this concept was explored by Wang & Smith (1995) and Dhole et al., (1996) but only gained popularity after 2000. The fixed load mass transfer processes can be converted to a fixed flowrate model when the outlet concentration is fixed at maximum; this is true in the absence of water gains and losses. Figure 2.13 depicts the separation of a water using process into a source and sink. Accordingly, the following definitions are adopted:

Water source: a water using process that supplies a certain flowrate, F_s, of water

Water sink/demand: a water using process that demands or consumes a certain flowrate, F_d, of water

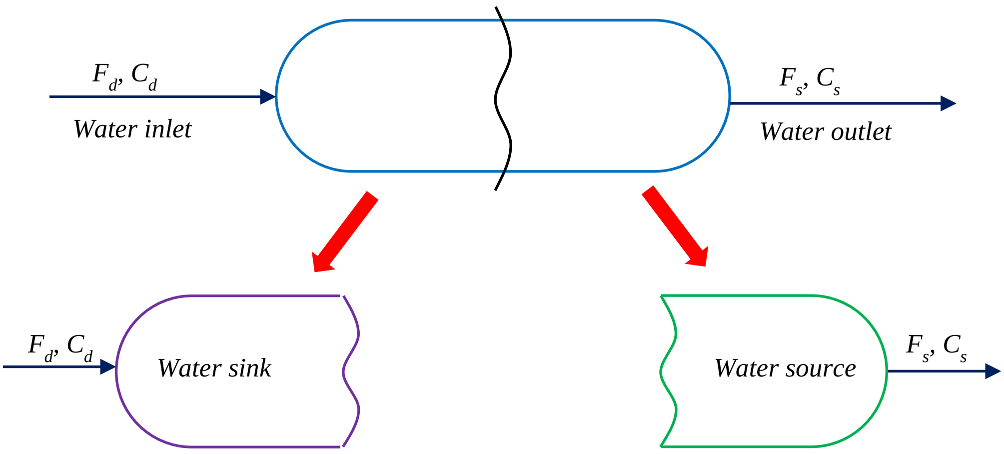


Figure 2.13: Division of mass transfer process into a source and sink (Poplewski et al., 2011)

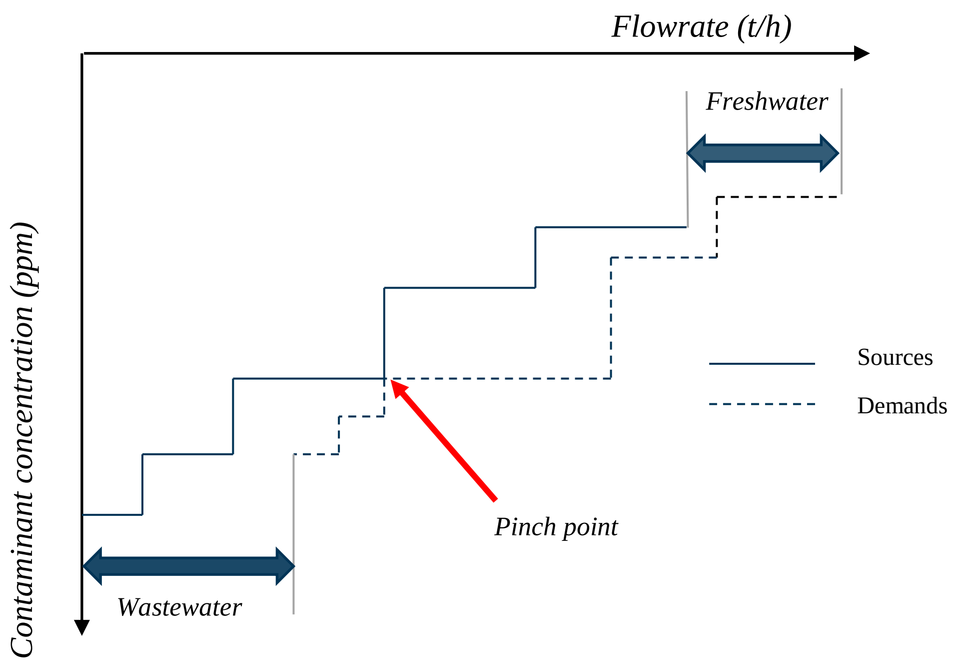


Figure 2.14: Water composite curve representation for the fixed flowrate approach (Dhole et al., 1996)

In a similar manner to Wang and Smith (1994), it is possible to develop a composite curve for non-mass transfer based units by separating them into sources and demands and developing a *combined demand composite plot* as shown in Figure 2.14. The overlap between the source composite and demand composite curves show the potential for reuse; the point of intersection is the pinch point. Insight from this curve can then be used to design a water network (Dhole et al., 1996). Unfortunately, when using this approach, mixing of streams may cause the pinch point to shift. Hallale (2002) developed a more robust means of locating the pinch and determining water targets. Thereafter, instead of using graphical means to design a water network, mathematical models can be used.

The fixed flowrate model avoids the details of the processes and considers only the water streams in a system. The inlet flowrate of water into a process need not equal the outlet flowrate i.e. water gains and losses are allowed. In fact, it is possible to consider processes that have only an inlet or outlet water stream, or multiple aqueous streams entering or leaving a unit. This allows the inclusion of non-mass transfer processes such as reactors, cooling towers and boilers (Teles et al., 2008).

The rise in popularity of the fixed flowrate approach since 2000 is due to the versatility of the approach coinciding with the increased emphasis on water conservation and the development of better mathematical solving techniques. This has made it possible to handle large complex problems in relatively short time with higher accuracy than in the past (Huang et al., 1999; Teles et al., 2008).

Complexity Associated with Water Network Optimisation

Nonlinearity in WNS problems generally arises due to bilinear terms, which result in nonconvexity. As previously described (Chapter 2.2), nonconvex problems present the possibility of obtaining multiple suboptimal solutions and nonoptimal stationary points. Any given feasible solution to a nonconvex problem is an upper bound of the true optimum. In order to improve the reliability of solutions and possibly verify its global optimality, relaxations are often performed in order to convexify the problem and provide the lower bound of the problem or starting point for the solution of the exact problem. The convexification transformation adopted is dependent on the nature of the nonlinearity. Transformations used in WNS are tailored to bilinear terms. One such example is the use of piecewise relaxation methods, such as the McCormick envelopes to relax the bilinear terms (McCormick, 1976). This method provides a lower bound for the original NLP problem, which can then be solved using a branch and bound solution procedure (Karuppiah and Grossmann, 2008; Quesada and Grossmann, 1995).

Meyer and Floudas (2006) applied a reformulation–linearization technique to a WNS problem. It involves the introduction of new nonlinear constraints, derived from the multiplication of constraints in the original model which are therefore redundant in the original model. The model is then linearized by replacing bilinear terms with the new RLT variables. Similar to piecewise-affine relaxation, this method provides a tight lower bound for spatial branch and bound optimisation.

Mathematical models of water treatment units are inherently nonlinear, and so increase the nonlinearity of the WNS problem. Many authors who have considered WRNS have avoided this increased nonlinearity by the use of black box optimisation. There is a trade-off between the simplicity of the problem and the accuracy of the results. By avoiding detailed regenerator models, there is the potential for the misrepresentation of the water network design.

Optimality in Water Network Problems

Due to the nonconvexity of the WNS problem, caution must be taken in order to ensure that any solution arrived at is not simply a local optimum. Savelski and Bagajewicz (2000) presented a paper on the optimality conditions for freshwater minimisation problems in single contaminant process plants. This work highlights characteristics of optimal solutions of WNS problems, based on the fixed load approach. Firstly, the contaminant concentration must be monotonic over any process that provides wastewater for reuse. This means that the inlet concentration for this process must not be lower than the outlet concentration. Secondly, the outlet concentration of head processes, those that only consume freshwater, is at its maximum possible concentration for the optimal network configuration. If this condition does not hold, the optimal solution has an equal objective function to when the maximum concentration condition is true.

The conditions presented by Savelski and Bagajewicz (2000) are valid in freshwater minimisation cases, and they can be used as a basis for linearisation of general WNS problems (Jeżowski, 2010). When attempting to solve WNS problems, it is common practice to either manipulate the structure of the problem, using methods such as linearisation or adopt a rigorous solution procedure in order to avoid suboptimal solutions.

Multicontaminant Modelling in Water Network Optimisation Problems

Multicontaminant modelling in WNS is additionally complex because it results in the introduction of more bilinear terms in the material balances at the mixing nodes. This in turn increases the nonconvexity of the model. It is possible to treat each contaminant individually, in which case convex and concave envelopes must be generated for each contaminant in order to convexify the problem (Quesada and Grossmann, 1995). Other works which consider each contaminant individually and use global optimisation techniques to solve the problem are Ahmetović & Grossmann (2011) and Chew et al. (2008). Faria and Bagajewicz (2010) introduce a binary variable to indicate which contaminant is treated in a particular treatment unit; this also increases the number of integer variables in the problem.

In order to avoid complexity, some works identify key contaminants and treat the problem as a single-contaminant case. The term key contaminant refers to the dominant contaminant. For mass transfer processes, Savelski and Bagajewicz (2003) proved that the condition of monotonicity holds for the key contaminants. The authors also established that at least one of the contaminants is at its maximum possible outlet concentration when water consumption is minimal.

Other works have combined contaminants into some kind of aggregate property or pseudo-component such as total dissolved solids (TDS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) salts and organics. This may allow the treatment of the problem as a single contaminant model, or at least reduce the number of contaminants (Bagajewicz and Faria, 2009; Khor et al., 2011; Smith, 2005).

According to Bagajewicz (2000), for the purposes of water minimisation pseudo-contaminant and key contaminant approached may be adequate. However, when regeneration is considered, the treatment type, unit design, energy consumption and treatment cost may be dependent on the nature of the contaminant. In this case it is important to treat each contaminant separately.

Solution Strategies for Water Network Optimisation Problems

Several solution strategies have been adopted in the solution of WNS problems in response to their complexity. Some of these will be highlighted below.

i) Linearisation

Direct linearisation involves the conversion of the nonlinear constraints to linear constraints. This can be done by making certain assumptions of values, thus converting bilinear expressions to linear expressions. For example, by fixing outlet concentration of the sinks at maximum or adopting the optimality conditions of Savelski and Bagajewicz (2003, 2000).This method of exact linearization is only applicable for mass transfer based operations.

In cases where non mass transfer processes, multiple contaminants or large-scale problems are considered, the reliability of a direct linearization is decreased. However, linearization can be used to generate a starting point for the solution of the exact problem. One such example is given in the work of Doyle and Smith (1997). In this work, the authors presented two formulations for the modelling of a mass transfer based problem. The nonlinear fixed mass load model was presented as the exact problem. It was initialised by solving a linear model with fixed outlet concentrations. If a feasible solution to the linear problem is found, this method results in a significant reduction in the computational time, and the chances of being stuck in local optima are reduced. The disadvantage of this approach is the possibility of eliminating stream connections in the initialisations that may otherwise lead to a better final solution.

This method can be improved by the use of a sequential procedure, by providing a good starting point, or an iterative approach. Gunaratnam et al. (2005) used a linear relaxation of the water networking problem is used to determine the network topology. Slack variables are introduced to the MILP formulation to represent the mass lost and gained in the mass transfer units. The flowrates obtained in the MILP are used in the LP formulation, whose objective is to minimise the slack and surplus variables. Concentrations levels are determined at this stage. These models are solved iteratively, until the convergence is achieved. The solution from the MILP-LP is used to initialise the full MINLP model. This sequential approach provides a more reliable solution, however global optimality still cannot be guaranteed.

ii) Stochastic/metaheuristic optimisation

A stochastic program is a mathematical program in which some of the parameters defining a problem instance are random (Grossmann, 2012). In WNS, uncertainty exists in the variability of throughput in respective units, the contaminant load from processes and the degree of contaminant removal in treatment units. Stochastic programming aims to synthesise a WN with one set of interconnections that is feasible over a range of values for these uncertain parameters. The handling of uncertainty in WNS was explored by Koppol and Bagajewicz (2003), who expressed the contaminant loads of the units as a probability distribution within a certain interval. Because the uncertain variables are continuous, the distribution results in an infinite number of constraints. The solution procedure therefore involves the discretisation, where a finite number of scenarios are considered. Unfortunately, for a finite number of iterations, stochastic methods cannot guarantee global optimality. A large number of scenarios are required in order to gain meaningful representation of the problem; however, this increases the associated computational expense. This trade-off is known as the *curse of dimensionality* (Khor et al., 2014).

iii) Deterministic global optimisation

This involves the use of global optimisation solvers, which generally decompose the MINLP into subproblems and solve them in a way that guarantees, often within some tolerance, that the solution is globally optimal. Modelling of WNS problems generally involves the development of a superstructure, which considers all feasible connections between water-using processes and water treating processes. Binary variables are used to activate only the optimal solution, which is a subset of these feasible solutions (Ahmetović and Grossmann, 2011; Karuppiah and Grossmann, 2006). Global optimisation solvers are advantageous as they often perform the necessary relaxation of the nonconvex problem.

Quesada and Grossmann (1995) presented a method for global optimisation of a water network problem that employed a *branch and bound framework* for the solution procedure. This required solution of both the exact problem and its convex relaxation, which are then successively updated until the optimum objective is identified. The convexification method used in this work is based on the reformulation-linearization technique for bilinear terms developed by McCormick (1976). The McCormick underestimators and overestimators for a bilinear term, $F^i x_j^i$, are given by Equations (2.7) to (2.10). Superscripts L and U represent the lower and upper bound of the respective terms.

$$F^i x_j^i \geq F^{iL} x_j^i + x_j^{iL} F^i - F^{iL} x_j^{iL} \tag{2.7}$$

$$F^i x_j^i \geq F^{iU} x_j^i + x_j^{iU} F^i - F^{iU} x_j^{iU} \tag{2.8}$$

$$F^i x_j^i \leq F^{iU} x_j^i + x_j^{iU} F^i - F^{iU} x_j^{iU} \tag{2.9}$$

$$F^i x_j^i \leq F^{iL} x_j^i + x_j^{iL} F^i - F^{iL} x_j^{iL} \tag{2.10}$$

The branch and bound framework is depicted in Figure 2.15, where *P* represents the nonconvex problem and *R* represents its convex relaxation. The lower bounds of the problem are computed by solving the convex relaxation of the original problem (Figure 2.15a). The upper bounds of a global minimum are obtained by the exact evaluation of the objective function within the feasible region (Figure 2.15b). The difference between the upper and lower bound is commonly known as the *relaxation gap*, *ε*, and it indicates the degree to which the upper bound can be guaranteed to be the global optimum. Both the upper and lower bounds are adjusted iteratively, until the relaxation gap is within an allowable tolerance. Branch and bound techniques are employed to update the value of the lower bound by partitioning the feasible region into a finite number of subregions. For each subregion, the upper and lower bounds are calculated and if a better value is obtained, the incumbent is fathomed (Figure 2.15c). The branch and bound search tree is depicted in Figure 2.15d.

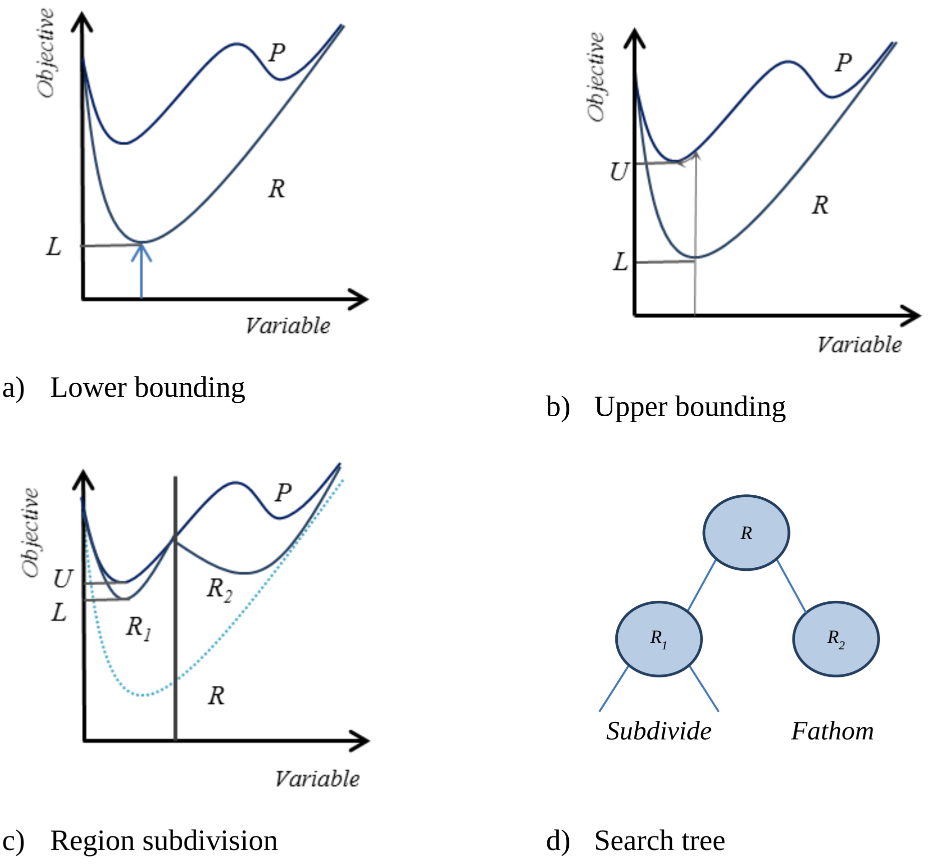


Figure 2.15: Spatial branch and bound procedure (Ryoo and Sahinidis, 1995)

The computational time required for a branch and bound problem is largely dependent on the quality of the convex relaxation. This, in turn, is determined by the upper and lower bounds of the variables involved in the nonconvex terms i.e. *complicating variables*. Effort is therefore often taken to contract these bounds using either *feasibility-based* or *optimality-based* range reduction techniques. Feasibility-based techniques use the structure of the constraints and the variable bounds to iteratively eliminate parts of the nonconvex problem that would be infeasible. Optimality-based techniques on the other hand, use the convex relaxation to eliminate regions where the objective function would be above the best known upper bound (Zamora and Grossmann, 1998). The application of these range reduction techniques to the general branch and bound framework results in the *Branch and Reduce Optimization Navigator* (BARON), a common solver for WNS problems (Ryoo and Sahinidis, 1996; Tawarmalani and Sahinidis, 2005). Other branch and bound based solvers include standard branch and bound (SBB), Lindo/LindoGLOBAL, Algorithms for coNTinuous / Integer Global Optimization of Nonlinear Equations (Antigone) and Cplex (GAMS Development Corporation, 2014).

Outer approximation is a convexification method that involves iterative linearizations that are accumulated and successively improved to result in a linear approximations of a nonlinear function. This forms an envelope, known as the convex hull, which underestimates objective function and overestimates the feasible region. Figure 2.16 shows the outer approximation performed at four points on a convex function, $f(x)$, with the starting point x_1. This method is used in the MINLP solver DICOPT. The problem is separated into a master MIP, where integer variables are fixed, and NLP subproblems which are linearized using outer approximation methods. The termination criterion for DICOPT is the absence of improvement in the NLP solution. This means that for nonconvex problems it possible to be trapped in local optima and global optimum cannot be guaranteed. It is therefore critical when using DICOPT to provide a good starting point for the algorithm (Duran and Grossmann, 1986).

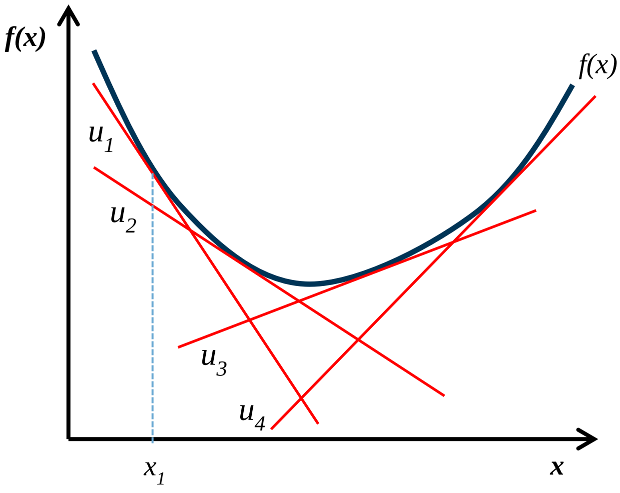


Figure 2.16: Outer approximation at four points of a convex function (Duran and Grossmann, 1986)

The *cutting plane theory* involves the introduction of linear inequalities, called *cuts*, as additional constraints to a problem, in order to discard unnecessary points in the feasible region. First, the problem is solved as an RMINLP, i.e. integer constraints are ignored. If an optimal solution is found at an integer point the algorithm terminates. Otherwise, a cut is made at integer point in the vicinity of the optimum; this reduces the size of the search space. Successive cuts are made such that, eventually, an integer solution is found (Kelley, 1960). This process is depicted in Figure 2.17, where the dot represents the optimal solution and the line represented the cut.

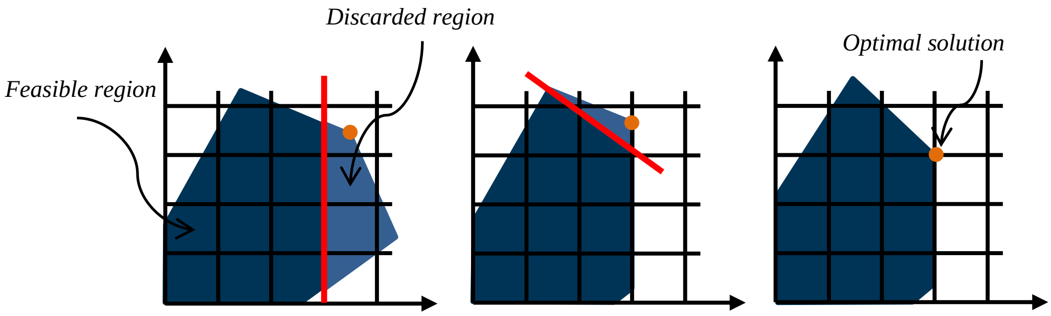


Figure 2.17: Cutting plane theory, showing successive cuts on a convex region (Kelley, 1960)

It is necessary to guarantee that the discarded regions do not contain the optimal solution; hence this method is best suited for convex problems. More specifically, global optimum is only guaranteed if all inequality constraints are convex and the equality constraints and objective function are linear (Pörn et al., 1999). Westerlund and Pettersson (1995) developed a solver based on the cutting planes theory called AlphaECP. For nonconvex problems, the cutting planes method works best when exact convexification techniques, such as the exponential and potential transformations, have been applied (Pörn et al., 1999).

2.4 Membrane Systems for Wastewater Treatment

While many non-membrane systems exist for the treatment of water, only membrane technologies will be considered in this work. Membrane technology has been used for use in water treatment since the 1970s, with the most common method being reverse osmosis (Water Environment Federation, 2006). Membrane technologies involve the purification of effluent by the transfer of water or contaminants across a permeable or semi-permeable membrane under the influence of a driving force. Different levels of purification can be reached depending on the driving force applied and the conditions of the membrane used. Figure 2.18 shows the different membrane technologies that can be applied to water regeneration. Each of these will be discussed briefly below.

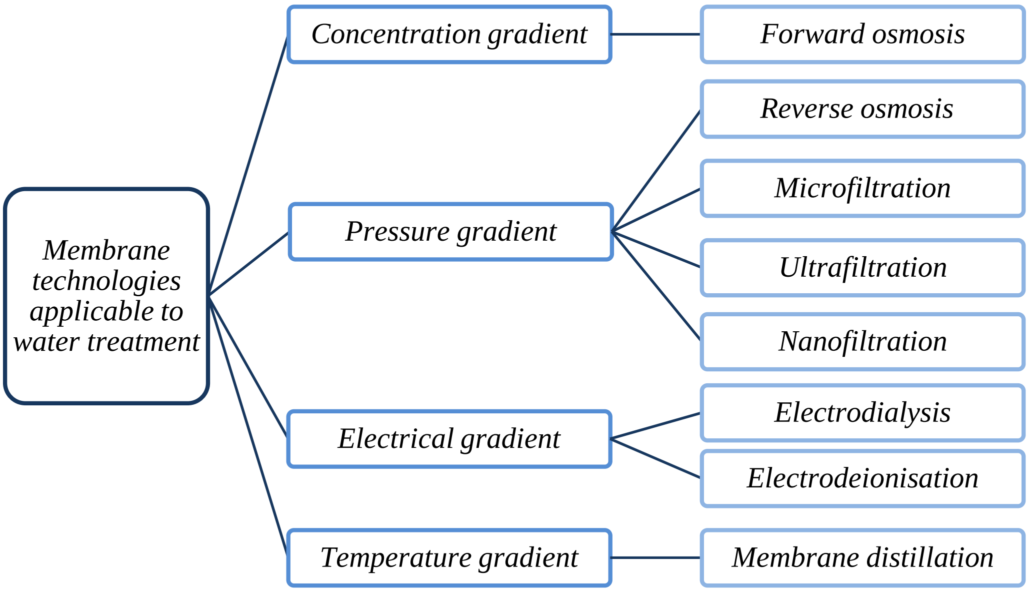


Figure 2.18: Classification of membrane technologies applicable to wastewater treatment according to the different driving forces

Forward osmosis (FO) is the movement of water molecules across a semipermeable membrane from a solution with a low contaminant concentration into a solution with a higher contaminant concentration until equilibrium is reached. Forward osmosis can be used in the treatment of industrial wastewater as well as sea water desalination, often as a pre-treatment for reverse osmosis (Cath et al., 2006).

Reverse osmosis (RO) is a modification of the forward osmosis process, in which a hydraulic pressure is applied to the system. The hydraulic pressure overcomes the osmotic pressure (resulting from the concentration difference) andthe pressure gradient between the solutions results in the mass transfer of solvent molecules from the concentrated solution to the less concentrated solution. Reverse osmosis is more widely used in water treatment than forward osmosis. RO membranes are capable of removing small organic molecules and dissolved ions, including monovalent ions (Lee et al., 2011).

Microfiltration (MF) is a physical process in which a solution is allowed to flow perpendicular to a porous membrane. The pores of the membrane range from 0.1 – 10 µm, such that any particles exceeding the pore size are retained on the membrane and thus filtered out of solution. This process is used, for example, in the clarification of fermentation broth or filtration of biologically treated waste water. MF is often used as a pre-treatment for UF, NF and RO (Fane et al., 2011).

Ultrafiltration (UF) is similar to MF, with a smaller pore size, 0.001-0.01µm. In addition to pore size, UF is characterised by its molecular weight cut off (MWCO), which is the molecular weight of the solute that achieves 90% rejection by the membrane. UF is used for the removal of bacteria, colloids, macromolecules and colloids from a solution (Water Environment Federation, 2006).

*Nanofiltration (*NF) is a high pressure process, involving membranes with subnanometer pore sizes (0.0001-0.001µm), capable of retaining some small organic molecules and dissolved ions. Nanofiltration membranes differ from reverse osmosis in that they have a low rejection to monovalent ions.

Electrodialysis (ED) is a process by which ions migrate across cation exchange and anion exchange permselective membranes under the influence of a direct electric current (Tsiakis and Papageorgiou, 2005). ED is most commonly used in the desalination of seawater, however, its popularity is slowly increasing for desalination in several food industries such as cheese, fruit juice and wine production.

Electrodeionisation (EDI) is an extension of electrodialysis that involves the addition of ion exchange resins to the membrane units. In the absence of ion exchange resins, ED systems are only able to process concentrated solutions. EDI therefore can be used for desalination of dilute solutions, without damaging the membrane (Strathmann, 2004a).

Membrane distillation (MD) is a process that employs a hydrophobic membrane and a difference in partial pressure, brought about by a temperature gradient, to result in the separation of two phases. This technology has the potential for use in water treatment; however, it is not widely used in industry for this purpose as yet (Alkhudhiri et al., 2012).

Other membrane processes that can be applied to water treatment include thermos-osmosis, pervaporation, and electrofiltration (Llamas et al., 2006). The abovementioned processes can be used in water treatment, either individually or in conjunction with other membranes either in series or parallel i.e. a membrane network. Figure 2.19 is presented to illustrate the effect of some membranes on water with a range of contaminants.

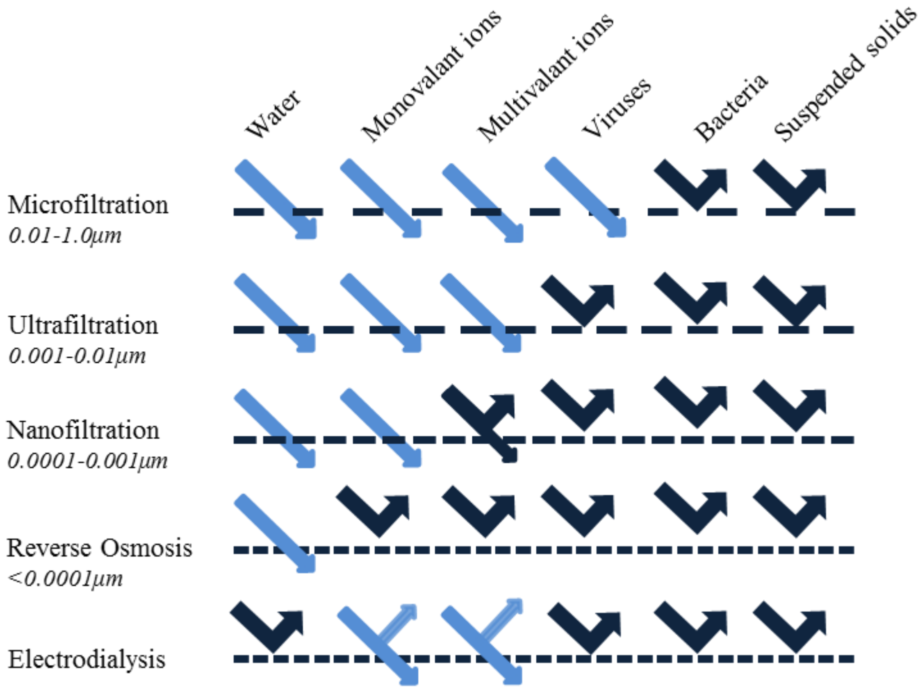


Figure 2.19: Illustration of the removal of common water contaminants by different membranes

2.5 Electrodialysis

The process of electrodialysis is based on the selective transport of ions from one solution to another through an ion exchange membrane under the driving force of an electrochemical potential gradient (Strathmann, 2004a)

2.5.1 Principle of Operation

An electrodialysis unit consists of a series of cation-exchange membranes (CEM) and anion-exchange membranes (AEM) alternately arranged between two electrodes; an anode which is positively charged and a cathode which is negatively charged. CEMs are negatively charged and allow the passage of cations, only. Similarly, positively charged AEMs allow the passage of anions only. A solution containing ionic species is allowed to flow in the compartments between CEM and AEM. Under the influence of a potential difference, cations from the solution are attracted toward the cathode and anions migrate towards the anode. However, due to presence of the alternately charged membranes, the flow of ions is selectively hindered. The result is an increase in the ion concentration in some compartments, and a corresponding decrease in ion concentration in adjacent compartments. The solution in the compartment that experiences an increase in concentration is commonly referred to as the *concentrate*; the solution with decreased concentration is known as the *diluate*.

Two orientations are possible for a large scale electrodialysis unit, the stacked design and the spiral-wound design. A membrane stack consists of multiple cell pairs, where a single cell pair comprises of a CEM, a concentrate compartment, an AEM and a diluate compartment (Strathmann, 2004b). Spacers are placed between membranes in a stack in order to separate the membranes and provide structural integrity. These spacers also serve the function of facilitating even mixing of the solutions in the stack. Figure 2.20 depicts the operating principle of an electrodialysis unit described above, in the form of a membrane stack.

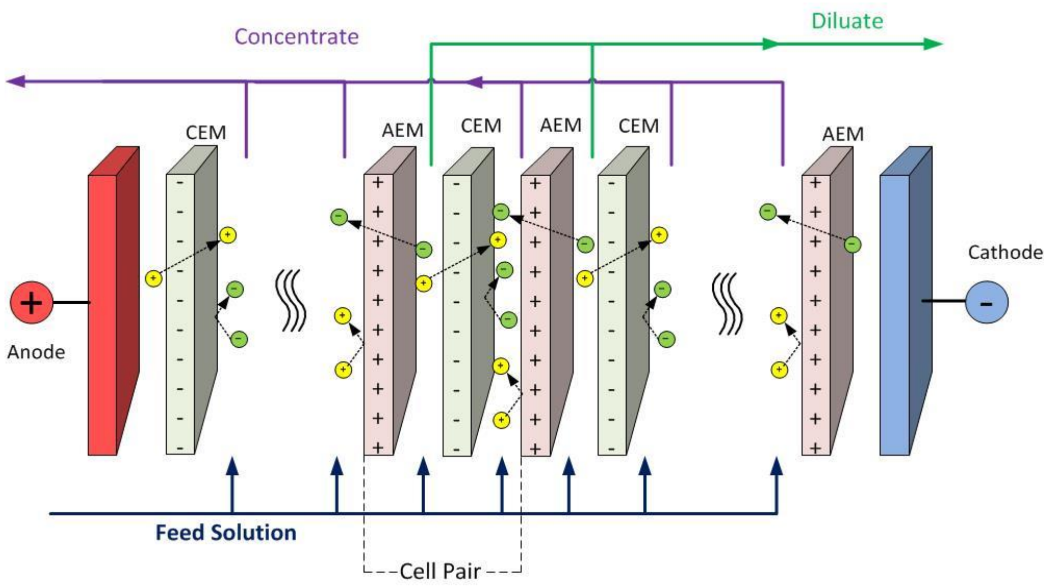


Figure 2.20: Schematic diagram illustrating the operating principle of electrodialysis

The use of multiple cell pairs between the electrodes increases the available ion exchange area, and in turn, this increases the number of ions that can be transferred for a given amount of energy. As a result, the stacked design is more energy efficient and less expensive than the spiral alternative.

Different modes of operation of the ED stack can be employed depending on the requirements of the system. For example, the ED unit may operate in batch, semi-batch or continuous mode and the diluate and concentrate streams may either flow co-currently or counter-currently. In order to improve the degree of desalination it is possible to increase the number of cell pairs, arrange multiple stacks in series or to have recycle streams within a single electrodialysis stack. The recycling of products back to the feed is known as feed and bleed operation, and is necessary in order to achieve a recovery rate greater than 50% (Strathmann, 2010). The arrangement of the spacers in a stack also depends on the application. Sheet flow spacers are arranged parallel to the membranes, and provide a short process path. Tortuous path spacers are arranged perpendicular to the membranes, in a serpentine manner, resulting in a longer residence time, at the expense of a high pressure drop.

Knowledge of membrane properties and their orientation as well as the properties of the fluids are essential to achieve technical and economic feasibility of the desalination process. Certain parameters, such as the conductivity and viscosity, are determined by the feed and product solution properties. Other properties can be varied within reasonable ranges in order to optimise the process; these include current applied voltage and current across the unit. The interdependence of these properties must be taken into account when developing mathematical expressions to describe the process of desalination (Strathmann, 2004c).

Current density is the electrical current applied per unit area. The relationship between applied voltage and current in ED, and consequently current density, is characterised by three regions. These regions are depicted in Figure 2.21 and described below.

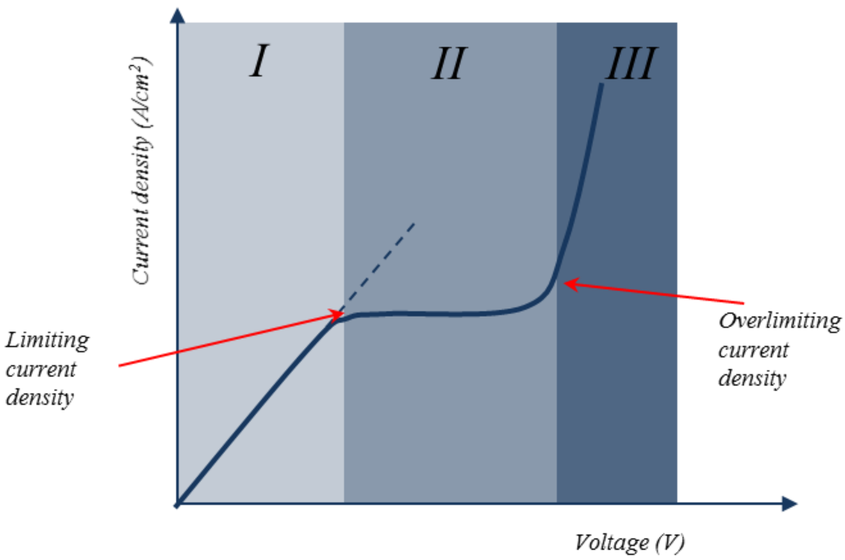


Figure 2.21: Diagram illustrating the relationship between applied voltage and current density in and electrodialysis stack at constant flow velocities and concentrations (Strathmann, 2010)

Region I: Current density is linearly dependent on applied voltage according to Ohms Law, and stack resistance is constant. This *Ohmic region* continues until a critical value known as *limiting current density*, i^{lim}, is reached. Ohms law states that:

$$Voltage = Resistance \times Current \ .$$

Region II: Once i^{lim} is reached, the cell resistance increases dramatically, and any increase in voltage does not result in significant change in current density. This is due to a phenomenon known as *concentration polarisation* as a result of the depletion of ions on the membrane surface in the diluate cell. This also corresponds with the accumulation of ions on the membrane surface in the concentrate cells, resulting in potential precipitation of salts and membrane fouling.

Region III: Continued increase in the applied voltage may result in the dissociation of water once a certain point, *overlimiting current density*, is reached. Beyond this point, increasing voltage leads to increasing current density (Strathmann, 2010).

For efficient operation of the ED unit, design and operating conditions must be selected such that limiting current density is not exceeded. This is the basis of many design and optimisation models (Lee et al., 2002; Tsiakis and Papageorgiou, 2005). Based on this, Strathmann (2010) presented an illustration of the relationship between the practically applied current density of an ED unit and the capital (membrane) and operating (energy) costs; this is shown in Figure 2.22. Optimisation is required to arrive at the best operating conditions, bearing in mind that the chosen current density must not exceed i^{lim}.

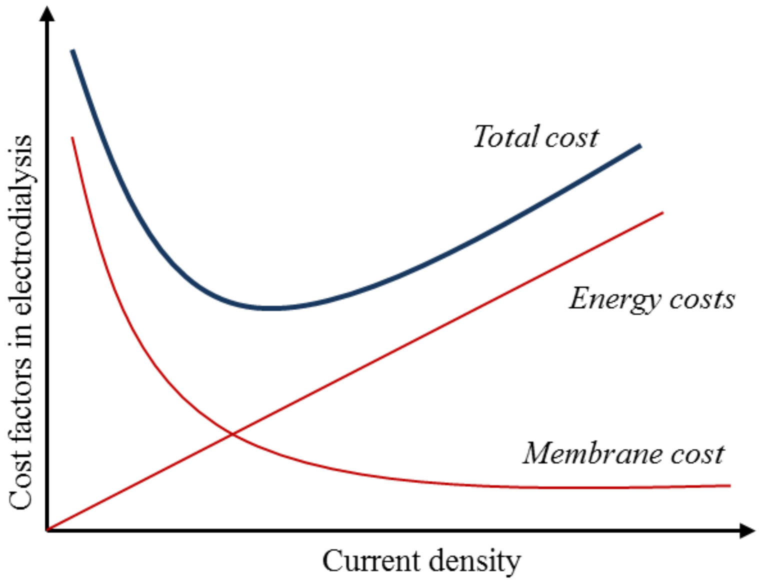


Figure 2.22: Illustration of the relationship between current density and electrodialysis cost factors (Strathmann, 2010)

2.5.2 Applications of Electrodialysis

Since the inception of electrodialysis as a water treatment technology, over 50 years ago, its applications have been extended to many different industries where an ultrapure product is required. Benefits of ED include the fact that it has few pretreatment requirements for ionic effluent, is operable at a wide temperature range, is easily adjustable to varying water quality feed and its membranes have high chemical and mechanical stability (Pilat, 2001; Strathmann, 2004b). The most common application is in the desalination of brackish water to produce potable water. Brackish water lies within a range of concentrations for which ED is advantageous over many other treatment processes, such as reverse osmosis i.e. from 1000 to 5000 mg/L. This is due to high water recovery rates and minimal fouling. Membrane fouling in ED is avoided by process reversal, where the polarity of the electrical potential is reversed at intervals, thereby removing any particles that may have adhered to the membrane surface. However, the main pitfall of ED in brine desalination is its inability to remove neutral toxic contaminants; this may necessitate pretreatment. (Strathmann, 2010)

Electrodialysis is commonly used for the demineralization of boiler water and desalination of effluent from process plants where ionic contaminants are predominant. ED is advantageous in process industries because recovery rates of 95% can be achieved and the units are able to operate at temperatures up to 50° C. Uses of ED in industrial processes include chloride removal in electrostatic precipitator dust of pulp and paper production and arsenic removal from electrolytes in hydrometallurgical applications (Dubrawski et al., 2015; Rapp and Pfromm, 1998a).

In the food and biotechnology industry, conventional electrodialysis has found several uses. One such example is the demineralization of whey protein, a by-product of cheese production. It contains harmful salts, but once demineralized, whey can be used for the production of baby foods and protein supplements. In this case, the operation of ED is often in batch or semi-batch mode (Greiter et al., 2002). ED is also being explored for use in tartaric wine stabilization, deacidification of fruit juices and amino acid removal from organic products (Oendodia, 2013).

The production of salt from sea water using electrodialysis has also been explored. Pre-concentration by ED results in a reduction of the amount of energy required for evaporation. In this event, sheet flow stack design is used. Salt production plants have been constructed in Japan using multiple membrane stacks with 3500 cell pairs per stack. It is possible to further process the diluate product to produce potable water (Turek, 2003).

In general, relative to reverse osmosis and nanofiltration, electrodialysis suffers from high energy consumption because electricity is required for the driving force of contaminant removal. This in turn results in higher operating costs than other membrane processes. Several efforts are being made in order to improve the efficiency of ED in order to make it more favorable. These include the development of electrodialysis-hybrid processes, and the optimisation of the existing process to improve energy efficiency.

2.5.3 Electrodialysis Related Processes

Electrodialysis can be applied with bipolar membranes resulting in the dissociation of water molecules which leads to the formation of a salt solution; an acid and a base. This process presents the advantage of minimising the amount of concentrate produced from a contaminated feed and the potential for production of useable chemicals (acids and bases) from industrial waste. Electrodialysis with bipolar membranes (EDBM) is often used in conjunction with conventional ED. Examples of applications include production of acids and bases from salts, acid recovery from fermentation products and pH control in chemical processes and at laboratory scale (Ghyselbrecht et al., 2014, 2013; Strathmann, 2010).

Continuous electrodeionisation operates under the same principles as conventional ED, however, the diluate compartments are filled with ion exchange resins, which serve to increase the conductivity in these cells. As a result, ultra-pure product can be achieved. The main disadvantage of this process is that the resins require regeneration, meaning that the process must be interrupted regularly to rinse the resins.

Research has also been directed at the improvement of ion exchange membrane properties, such as the reduction of resistance, increase of chemical stability and higher selectivity. Energy consumption can also be reduced by conductive spacers, this concept has been applied at laboratory scale (Strathmann, 2010).

2.5.4 Electrodialysis Modelling and Optimisation

Korngold (1982) conducted an experimental investigation to determine the effect of certain design parameters on the amount of energy required in ED, as well as deriving a simplistic calculation method for the energy consumption. The author identified the key parameters in ED as current density, membrane resistance, cell thickness, spacer type and brine concentration. In this work, Korngold (1982) highlighted features necessary to achieve optimal construction of an ED unit. These can be summarized as follows:

(i) Diluate cells must be thin;
(ii) Minimal pressure difference between diluate and concentrate cells must be maintained for mechanical stability;
(iii) Construction materials for cells and membranes must provide mechanical integrity and structural stability;
(iv) Cells must be constructed to prevent internal and external leakage; and
(v) Pressure drop across the unit must be minimised.

For the development of a sound mathematical model to accurately describe the functioning of an ED unit, it is necessary to take the above named factors into account.

Kraaijeveld et al. (1995) developed a mathematical model to describe the operation of a batch-mode electrodialysis unit. This model was based on the diffusion of ions across the membranes. This model employed Maxwel-Stefen equations to represent the mass transfer resistances of the membranes and the diffusion films on either side of the membranes. The major pitfall of this model is that the necessary diffusion coefficients of the membranes are not readily available in literature. The determination of membrane properties in this work was conducted experimentally. This model considered only diffusive transport, and did not consider other transport mechanisms.

Nikonenko et al. (1999) presented a model for the cost analysis of the convective-diffusion model for electrodialysis, based on the work of Sonin and Probstein

(1968). This model, applied to continuously operated ED units, considers the convection of fluids and the diffusion of ions across the membranes. One of the main assumptions was the absence of spacers in the unit. The cost function combined the operating cost of desalination and pumping with the capital and membrane replacement cost.

Lee et al. (2002) published an extensive study on the steps taken to design an electrodialysis using a model based on the current density of a unit. This approach avoids the need for experimental determination of diffusion coefficients. Some assumptions regarding the flow characteristics of the fluid were made, resulting in the avoidance of experimental determination of diffusion coefficients. These assumptions are as follows:

(i) Operation is ohmic, i.e. current density during operation must not exceed limiting current density;
(ii) The concentration potential difference between the concentrate and diluate are negligible relative to the voltage drop due to the ohmic resistance of the solutions;
(iii) Water transport across the membranes is sufficiently small relative to the solution flowrates and is therefore negligible;
(iv) Back diffusion of ions across the membranes is negligible; and
(v) Changes in ohmic resistance of the solutions are negligible due to boundary layer effects.

Based on these assumptions, a detailed derivation of the design equations for an electrodialysis unit was presented. The foundation for the model is the description of the degree of desalination, dC^{Δ}, with respect to the rate of change of cross sectional area, dA. This expression, given by Equation (2.11), is derived from Faradays Law.

$$dC^{\Delta} = \frac{iN\zeta}{zFQ^{d}} dA \tag{2.11}$$

Where: i = Electrical current density

N = Number of cell pairs

z = Electrochemical valance

F = Faraday number

Q^d = Diluate flowrate

A = Cross sectional area

C^{Δ} = Concentration flux

ζ = Current efficiency

Building on Equation (2.11), the authors derived expressions for the applied area, voltage, current, and the amount of energy required for desalination. This model was developed for a unit operating in continuous mode, capable of the desalination of brine, i.e. NaCl.

The work of Lee et al. (2002) was extended by Tsiakis and Papageorgiou (2005), who developed a model for multi-stage electrodialysis, adopting feed and bleed operation. Again, this work was for continuous, single-contaminant desalination. An optimisation model, according to the framework described in Chapter 2.2 (p2-12), was presented, for the minimisation of the costs of ED. The objective function, given by Equation (2.12), combined the capital cost and operating costs. The capital cost is dependent on the total required membrane area and operating costs are based on the total desalination and pumping energy requirements per annum.

$$K_{ED} = \frac{k^{mb}}{t^{max}} \sum_s A_s + t^d k^{el} Q^p \sum_s \left(E_s{}^{des} + E_s{}^{pum} \right) \tag{2.12}$$

Where: A_s = Membrane area per stage, s

k^{mb} = Membrane cost factor

t^{max} = Maximum life span of the unit

E_s^{des} = Desalination energy per stage, s

E_s^{pum} = Pumping energy per stage, s

Q^p = ED throughput

t^d = Annual operating time

k^{el} = Unit cost of electricity

Brauns et al. (2009) experimentally verified the current density-based model presented by Lee et al. (2002). A comparison was conducted between the model predictions and laboratory scale experiments as well as a pilot scale ED plant. It was concluded that the model is an acceptable estimation of optimal stack geometry, provided that operation remained within the ohmic region, as per the assumption. This work also identified 5 main limitations of the current design model, i.e.

(i) It is only capable of handling single contaminant feeds, where the electrolyte is a simple symmetrical salt;

(ii) It is based on the assumption that the equivalent conductivity is independent of the concentration of salt in the unit;

(iii) The concentrate and diluate flowrates are assumed to be equal;

(iv) Only concurrent operation is considered; and

(v) The diluate and concentrate compartments are assumed to be geometrically similar (i.e. the compartment widths).

2.6 Water Network Optimisation with Partial Regeneration

Water regeneration network synthesis can be modelled using water pinch techniques or mathematical superstructure based optimisation. Hallale (2002) presented a method for determining regeneration options using graphical methods. By considering water surplus and deficit over the different units in a system a surplus diagram can be drawn indicating regeneration potential in the following three regions, where "*pinch purity*" is the purity of the process stream at the pinch.

Above the pinch. Water sources already above pinch purity are treated and upgraded. This can reduce freshwater consumption.
Across the pinch. Water sources below the pinch purity are upgraded to concentrations above the pinch. This takes water from surplus region into deficit region, potentially reducing both freshwater consumption and wastewater production.
Below the pinch. Water sources below the pinch purity upgraded, resulting in concentrations below pinch purity; this does not affect freshwater consumption.

The success of water regeneration networks using graphical methods is therefore highly depended on accurate identification of the pinch point. For this and previously mentioned reasons, synthesis of water networks involving water regeneration units is most commonly performed by mathematical optimisation techniques. Design models for treatment units are generally nonlinear and often nonconvex; therefore, their inclusion in WNS problems may increase computational complexity. As such, it is common practice to describe regenerators by using a simple recovery expression, rather than considering the detailed design of a regeneration unit. This approach is often referred to as the "*black box"* approach.

2.6.1 Water Network Optimisation with Black Box Regenerator Models

The black box simplification allows the design of complex networks comprising multiple water sources and sinks as well as multiple regenerators. In systems where multiple regenerators have been considered, the different treatment processes are differentiated by varying the removal ratio. An comprehensive example of this is given in the work of Khor et al. (2012). In this work, a network of membrane and non-membrane treatment processes was developed within the water network. Recycling of treatment products, where practical, was allowed, otherwise, binary variables were used to prevent impractical connections. The cost function included only the capital cost of the individual regeneration units; operating costs were assumed negligible. The regenerator capital cost was expressed as a single value, independent of the size or capacity of the unit.

In the work of Chew et al. (2008), a single regenerator was considered for the treatment of multiple contaminants from multiple integrated plants. The cost of regeneration is represented by the sum of capital cost of a unit, a linear function of throughput, and operating cost, a linear function of load removed. Tan et al. (2009) employed a linear function for the cost of regeneration, multiplying an arbitrary dimensionless number by the throughput of the regenerator. In this work, Tan et al. (2009) presented a sensitivity analysis, indicating that the choice of the value of this constant may determine whether or not the regenerator exists. It is therefore important to accurately calculate the cost of regeneration in order to avoid misrepresentation of the optimal network configuration.

Faria and Bagajewicz (2010) presented a nonlinear cost function for the capital cost of regeneration, given in Equation (2.13).

$$TAC_r = \sum_r OPN_r FR_r + af.CCR_r(FR_r)^{0.7} \tag{2.13}$$

Where: TAC_r = Total annualised cost of regenerator r

OPN_r = Operating cost of regeneration process r

FR_r = Total flowrate through regeneration process r

af = Annualisation factor

CCR_r = Capital cost factor of regeneration process r

While this is more representative of cost than the linear expression, it still does not differentiate between the costs of different treatment types. It also does not capture the dependence of cost on all the design aspects of the unit (Kim, 2012).

Other examples of black box models can be found in the works of Ahmetović & Grossmann (2011), Almaraz et al. (2015), Bagajewicz & Faria (2009), Faria & Bagajewicz (2010), Galán and Grossmann (1999) and Karuppiah & Grossmann, (2006).

2.6.2 Water Network Optimisation with Detailed Regenerator Models

Galán and Grossmann (1999) developed an NLP for the optimisation of a water treatment network. The objective was to determine the optimal allocation of multiple effluent streams to different treatment units that would enable the combined discharge to meet the composition regulations at minimum cost. This was achieved by minimising the throughput of the treatment units subject to material balance constraints and regenerator removal ratio expression. The superstructure of the treatment network is depicted in Figure 2.23.

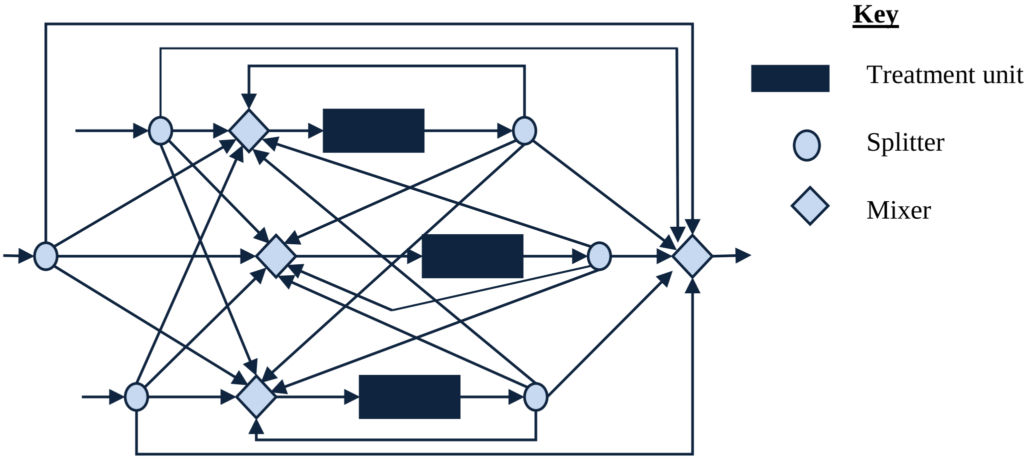


Figure 2.23: Water treatment network superstructure from the work of Galán and Grossmann (1999)

The treatment process considered in this work, for all regenerators present, was non-dispersive solvent extraction (NDSX). A shortcut model, comprising a single equation, that relates the regenerator feed to the product was presented (Ortiz et al., 1996). This expression was used to calculate the degree of contaminant removal, instead of fixing it at a constant value. The design of the treatment unit was not considered.

Khor et al. (2011) presented an MINLP for the optimisation of a water regeneration network. In this work, a water network comprising multiple sources and sinks was combined with a detailed design model of a single reverse osmosis

(RO) unit. The model was designed to handle multiple contaminants; this was achieved by including an expression for regeneration cost that is independent of contaminant type adopted form the work of El-Halwagi (1997). The overall objective was expressed as a cost function, which involved the minimisation of freshwater consumption, wastewater production and regeneration cost. The superstructure used in the work is depicted in Figure 2.24.

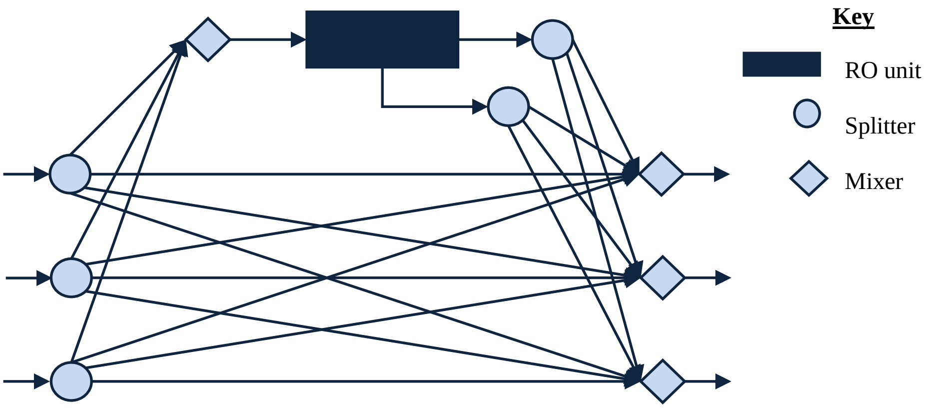
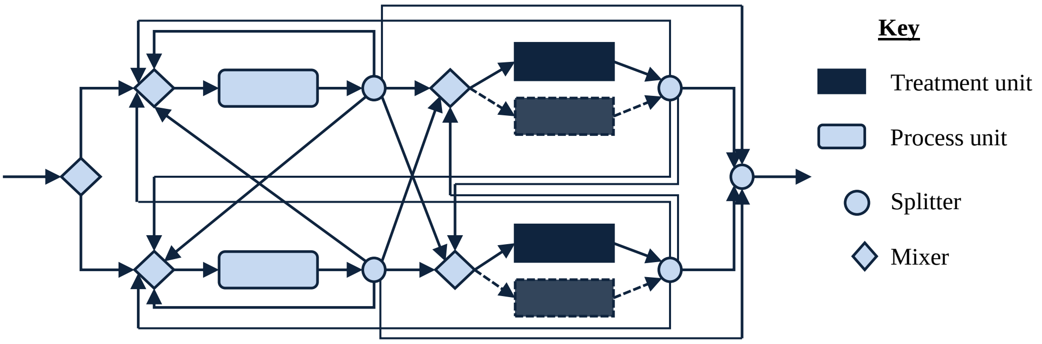


Figure 2.24: Water network superstructure from the work of Khor et al.(2011)

Yang et al. (2014) developed an MINLP for a water network containing multiple water using processes and multiple water treating units. The problem, which was modelled using general disjunctive programming (GDP) is an extension of similar models presented by Ahmetović and Grossmann (2011) and Karuppiah and Grossmann (2008, 2006). It can be depicted in the superstructure shown in Figure 2.25. Each treatment unit was described by a shortcut design model, the purpose of which was to provide an accurate relationship between regenerator feed and product. Both membrane and non-membrane water treatment methods were considered, including reverse osmosis, ion exchange resins, sedimentation, activated sludge, trickling filter and ultrafiltration. The objective was to minimise the freshwater consumption, regeneration cost and cost of cross-plant piping. The operating and capital costs of treatment were fixed, and therefore independent on the design and throughput of the unit.



**dashed lines indicate alternative treatment units*

Figure 2.25: Water network superstructure from the work of Yang et al.(2014)

The use of short cut models avoids the complexity of regenerator design models while allowing the synthesis of membrane networks with more accuracy than black box assumptions. This compromise if often referred to as grey box modelling.

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3

MODEL DEVELOPMENT

3.1 Introduction

This chapter outlines the development of the integrated water and energy minimisation model. Firstly, a detailed exploration of the considerations for multicontaminant modelling is given, based on the conditions present and required in an electrodialysis (ED) plant and preferable modelling techniques in water network synthesis (WNS). Emphasis will be placed on the considerations for a binary mixture of salts. This is followed by the detailed derivation of a multicontaminant electrodialysis energy-minimisation model. Two alternative ED models are presented, making different assumptions about the solution conductivity. Finally, the water network optimisation constraints are described, including the interactions between the WNS and the ED design model.

3.2 Considerations for a Multicontaminant System

With respect to both ED design and WNS there are considerations that must be made when developing a multicontaminant model, mainly, concentration and conductivity. Alternate approaches to the expression of these two variables are explored in the following section.

3.2.1 Concentration

Multiple approaches for the representation of contaminant concentrations were considered. These approaches, which are based on general multicontaminant modelling, common WNS modelling practice and logic, were evaluated for their suitability to both ED design and the background process, WNS. These are the key contaminants, pseudo components, average concentration and equivalent concentration.

i. Identifying a Key Contaminant

This is a common approach in water network synthesis for multicontaminant problems (Li and Chang, 2007; Savelski and Bagajewicz, 2003; Wałczyk and Jeżowski, 2008). It assumes that one species is of significant quantity in the solution and as such, the effects of the other contaminants are negligible. It is best suited in situations where a known contaminant is in abundance. All parameters used in modelling are based on that specific contaminant and the modelling constraints would remain the same as for a single contaminant system (Savelski and Bagajewicz, 2003). In the case of electrodialysis, the key contaminant assumption is often made when dealing with the desalination of brine or seawater where sodium chloride is known to be in abundance (Brauns et al., 2009; Lee et al., 2002; Tsiakis and Papageorgiou, 2005). However, for the consideration of ED as part of a water network, this technique is not appropriate, as the abundant contaminant is not known *a priori*. It is therefore necessary to ensure that the model is capable of handling several contaminants at varying concentrations. The feed concentrations to the ED are determined by the optimisation model and so selecting a key contaminant may lead to inaccuracies. Furthermore, this assumption would limit the applicability of ED as a separation tool within the water network. The key contaminant approach may also underestimate the energy requirement and unit design variables as these are determined by the nature of the contaminants in solution, i.e. valence and stoichiometric coefficients.

ii. Aggregate Properties/ Pseudo components

It is common in WNS to group all or some contaminants into certain aggregate properties such as the total load, total dissolved salts (TDS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total salts, organics etc. (Bagajewicz and Faria, 2009; Khor et al., 2011). This allows the effluent to be treated as a single contaminant problem or at least reduce the number of contaminants. This summed load would then be used to determine the design parameters of the treatment unit. This approach is also common in membrane processes that are dependent on particle size and overall concentration only. While this simplification would take into account all the contaminants, as opposed to the key contaminant approach, it does not consider the fact that different ions behave differently within the ED unit. This difference in operation is brought about by the interactions between the ions, and between the ions and the membranes. For example, similarly charged ions with different radii may have different transportation rates across a particular membrane, depending on the size of the membrane pores. It is therefore important to consider the different ions separately.

iii. Average Concentration

This approach involves calculating a simple average concentration based on the concentrations and the number of contaminants in the feed solution. Similar to the total load, the average concentration would neglect the effect of different contaminants on the rate of removal (Strathmann, 2004c). A fatal flaw of this approach is it would underestimate the current required for desalination.

iv. Equivalent Concentration

The equivalent concentration is a means of calculating the concentration of an ionic solution. It involves the summation of the contaminant concentrations weighted by the stoichiometric coefficient and valence of each ion. The equivalent concentration, C_{eq}, is calculated using either the anion or cation valences or both. This relationship is given in Equation (3.1) below, where z denotes the valence and v, the stoichiometric coefficients (Strathmann, 2004b). The subscripts *salt*, *cat* and *an* refer to the salt solution, cation and anion respectively.

$$C_{eq} = \sum_{salt} \frac{|z_{cat}v_{cat}| + |z_{an}v_{an}|}{2} C_{salt} = \sum_{cat} z_{cat}v_{cat}C_{salt} = \sum_{an} z_{an}v_{an}C_{salt} \qquad (3.1)$$

This approach has the advantage of truly representing the contribution of each of the ions to the total solution concentration by taking into account the ionic valence and stoichiometric coefficient. The equivalent contaminant approach is most appropriate for multicontaminant modelling of an electrodialysis unit (Strathmann, 2004b).

3.2.2 Conductivity

Conductivity is a property that describes the ability of a solution to conduct electricity by relating the current flowing in a solution to the potential difference across it, as well as the number of ions in solution (Wright, 2007). Given that ED is an electrically driven process, accurately depicting conductivity is imperative to the design of an electrodialysis unit. For the single contaminant model developed by Lee et al. (2002), a constant value for the solution conductivity was assumed. This assumption was valid because NaCl presents a relatively weak relationship between concentration and conductivity, so the fluctuation of conductivity with concentration is negligible. As such, the conductivity was assumed to take a single value for the entire range of concentrations within the ED.

When considering multiple contaminants, the dependence of conductivity on the nature of contaminants cannot be ignored. This is because the strength of interactions between the ions has a significant impact on a solution’s ability to conduct an electrical charge (Anderko and Lencka, 1997). As such, modifications must be made to the model to calculate the conductivity of the solution based on the proportion of ions in the solution. Due to the fact that this proportion is determined as a result of the optimisation, the conductivity calculation must be embedded into the model.

The accurate calculation of solution conductivities involves the application of a series of relationships between concentration and conductivity. The complexity of these relationships increases as the number of contaminants and the ionic valences are increased (Bianchi et al., 1989). However, this requires the knowledge of ionic conductivities, which are not available in literature for a wide range of contaminants. Alternatively, solution conductivity can be determined empirically. Experimental determination accurately captures the ionic interactions. Regression can be applied to these results to develop equations which can be included into the optimisation model. The following sections describe analytical and empirical methods for determining conductivity, with an emphasis on binary systems.

i. *Analytical Determination of Conductivity*

The Deybe-Hückel-Onsager equation gives the relationship between the molar concentration of a particular contaminant and its equivalent conductivity. This expression is applicable only to simple and mostly symmetrical salts (Wright, 2007). Equivalent conductivity, Λ, for an electrolyte with concentration, C, is given by Equation (3.2).

$$\Lambda = \Lambda^\circ - (A + B\Lambda^\circ)\sqrt{C} \tag{3.2}$$

Where Λ^o is the electrolyte conductivity at infinite dilution, this value can be acquired from literature (Haynes, 2014). The constants A and B are dependent on temperature, valence and viscosity. For dilute solutions at 25°C they can be related to the valence as follows: (Wright, 2007):

$$A = 60.58\, z^3 \tag{3.3}$$

$$B = 0.22293\, z^3 \tag{3.4}$$

Considering a mixture of only two salts, the individual conductivities, κ_x, are combined to result in the solution conductivity using the mixing relationship for binary systems described by Anderko and Lencka (1997).

$$\kappa = \sum_{x=1}^{2} a_x \kappa_x \tag{3.5}$$

In this expression, κ refers to the specific conductance of the solution or the individual components. The relationship between specific conductance and equivalent conductivity is given by Equation (3.6) (Strathmann, 2004b).

$$\Lambda = \frac{\kappa}{C\left(z_{cat}v_{cat} + \left|z_{an}v_{an}\right|\right)} \tag{3.6}$$

This expression can be applied to both the individual electrolytes and the overall solution. The combination of equations (3.2)-(3.6) allows one to calculate the conductivity of a binary mixture of electrolytes given their individual concentrations and infinite conductivities. For more complex mixtures, other concentration-conductivity expressions that account for the ionic strength and temperature must be applied (Bockris and Reddy, 1970; Fuoss and Accascina, 1959; Wright, 2007)

ii. Empirical Determination of Conductivity

In some cases, the analytical approach may not be applicable, for example, if the relevant parameters are unavailable or the solution concentrations lie beyond the range of applicability of the equations. In addition, systems with more than two components, Equation (3.5) for mixing cannot be applied. Anderko and Lencka (1997) describe an intricate method for calculating conductance of ternary systems; it is dependent on the ionic strength, which is determined experimentally. As the complexity of the system increases, these equations decrease in reliability.

An alternative method for complex systems is to determine the conductivity experimentally over a range of concentrations and use regression to embed this information into an optimisation model. For some common combinations of salts, this information is available in literature (Anderko and Lencka, 1997; Bianchi et al., 1989; Stearn, 1922).

An example of this is shown in Figure 3.1, for a solution of NaCl and $MgCl_2$. A linear regression of the relationship for a 0.5 fraction of NaCl gives the following expression:

$$\Lambda = -3.3708\ C^{1/2} + 10.986 \tag{3.7}$$

This expression can be embedded into the design model to give the accurate conductivity at the ED feed concentration. The choice between the empirical and analytical method for representation for equivalent conductivity is dependent on the availability of information in the particular case.

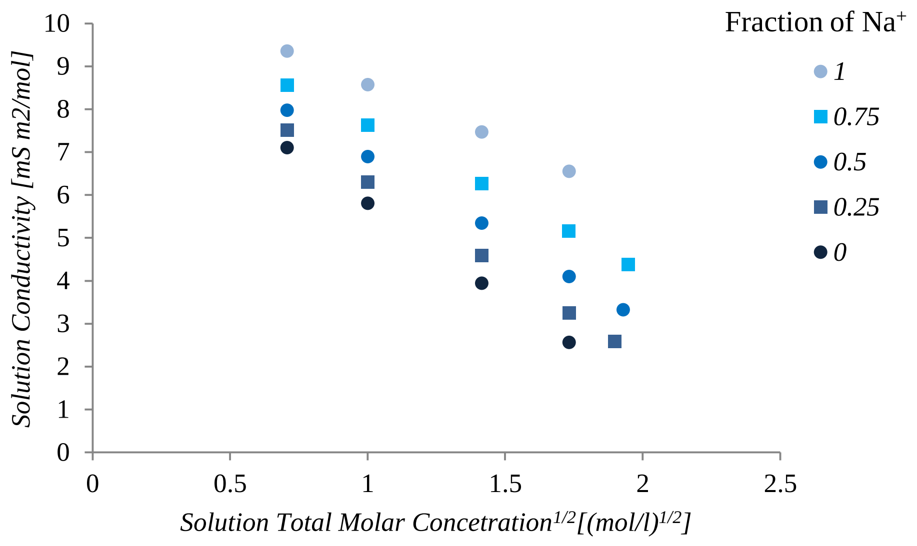

Figure 3.1: Solution conductivity for a mixture of NaCl and $MgCl_2$ at varying concentrations (Bianchi et al., 1989)

3.3 Electrodialysis Design Model

The multicontaminant ED optimisation model in this work was developed based on the procedure adopted in the single contaminant ED design model presented by Lee et al. (2002). The modelling of electrodialysis units is inherently complex because the degree of contaminant removal is directly dependent on the type and size of the contaminants in question. More specifically, due to the fact that the ED operating mechanism involves the migration of electrons, the performance of the unit is affected greatly by the number of electrons in the solution i.e. the valence of ions. The strength of the interactions between ions plays a significant role, especially for more complex ions; these interactions may either enhance or inhibit the rate of transfer of ions. As such, the multicontaminant model was developed by modifying the single contaminant model, taking into account all the above-mentioned concerns.

Emphasis was placed on addressing the limitations of the existing ED design model identified by Brauns et al (2009). The two factors addressed in this work are as follows:

(i) This work considered a multicontaminant feed.

(ii) The solution conductance has previously been expressed as a linear function, in which the equivalent conductivity is a constant value and is independent of the solution concentration. In this work the conductivity is presented as a function of concentration of the contaminants in the solution.

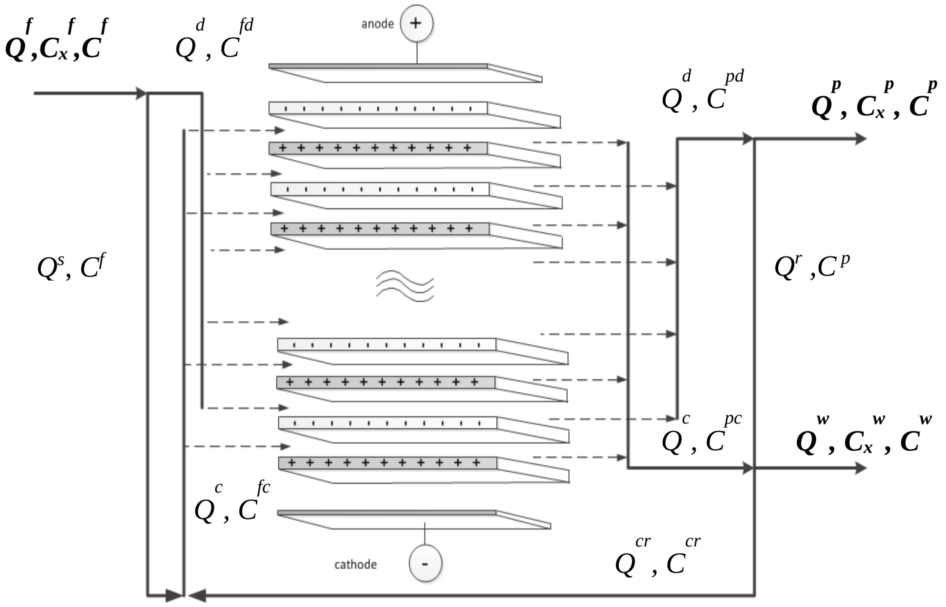

Figure 3.2: Schematic layout of a single stack electrodialysis unit

The ED models described in this work were based on the stack design depicted in Figure 3.2. The feed and bleed operation mode allows the potential recycling of both concentrate and diluate streams. This increases the overall contaminant removal rate and minimises water transport across the membranes via osmosis.

3.3.1 Problem Statement

The problem statement for the standalone ED model can be summarised as follows:

Given

(i) Plant design specifications i.e. plant capacity, Q^f, feed concentrations, C_x^f, product concentrations C_x^p;

(ii) Costing parameters i.e. membrane cost, k^{mb}, electricity cost, k^{el}, annual operating time, membrane life span; and

(iii) Operating parameters including cell width, infinite conductivities, $\Lambda_x°$ operating efficiencies, practicality coefficients and empirical constants

It is required to determine

(i) Optimal plant design variables including area, length, number of cell pairs; and

(ii) Optimal operating conditions including desalination energy, pumping energy, current and voltage such that capital and operating costs are minimised.

3.3.2 Assumptions

The model was developed based on the following assumptions:

i. The ED unit is modelled as a single stage plant according to the configuration depicted in Figure 3.2;
ii. The concentrate and diluate compartments are geometrically similar and the fluids in the respective streams have identical flow patterns;
iii. The concentrate and diluate flowrates are equal and uniform, this is achieved by the use of spacers;
iv. The fluids in the concentrate and diluate compartments flow co-currently;
v. Electron transfer is in the ohmic region, implying that the operating current density must not exceed limiting current density;
vi. Concentration potential due to the different concentrations is assumed to be negligible compared to the voltage drops due to the ohmic resistance of the solutions;
vii. Boundary layer effects on the ohmic resistance of the solutions is negligible;
viii. The thickness of the membrane is considered negligible relative to the length of the ED unit;
ix. Concentration of salt species are expressed in terms of molar equivalents;
x. Water transport across the membranes is negligible, compared to the total flowrate of water in the cells;
xi. The feed is comprised a binary mixture of salts; and
xii. Membrane resistances are independent of the salt solution.

3.3.3 Electrodialysis Nomenclature

Below is a list of the parameters and variables used in the development of the electrodialysis model.

Sets

X	$\{x \mid x$ is an ionic contaminant$\}$

Electrodialysis Design Parameters

A,B	Equivalent conductivity constants
a_x^d, a_x^c	Fraction of contaminant, x, in the diluate or concentrate stream
C_x^f	Feed concentration of each contaminate x, keq/m^3
C_x^p	Product concentration of each contaminate o, keq/m^3
F	Faradays constant, As/keq
k^{el}	Cost of electricity, \$/kWh
k^{mb}	Cost of membrane, \$/m^2
k^{tr}	Conversion factor, MJ/kWh
t^d	Total annual operating time , s/annum
t	Maximum life span of the plant, years
$v_{a,c}$	Stoichiometric coefficient of an anion or cation
w	Membrane width, w
$z_{a,c}$	Electrochemical valance of an anion or cation
z_x	Valence of coefficient, x
α	Shadow factor
β	Volume factor
δ	Cell thickness, m
ε	Safety factor for correction of limiting current density
ζ	Overall current efficiency
η	Pumping efficiency
Λ_x^o	Infinite equivalent conductivity of salt x, Sm^2/keq
μ	Fluid viscosity, kg/sm

ν_x	Stoichiometric coefficient of contaminant, *x*
$\rho^c+\rho^a$	Total resistance of cation exchange and anion exchange membranes, Ωm^2
σ	Limiting current density constant, As^bm^{1-b}/keq
τ,ω	Concentrate concentration constants
φ	Limiting current density constant

Electrodialysis Design Variables

A	Total unit area, m^2
C^c	Equivalent concentration at any point in the concentrate stream, keq/m^3
C^{cr}	Equivalent concentration of concentrate recycle, keq/m^3
C^d	Equivalent concentration at any point in the diluate stream, keq/m^3
C_{eq}	Equivalent concentration of salts in ED unit, keq/m^3
C^f	Equivalent concentration of the ED feed, keq/m^3
C^{fc}	Equivalent concentration of concentrate feed, keq/m^3
C^{fd}	Equivalent concentration of diluate feed, keq/m^3
C^p	Equivalent concentration of the ED product stream, keq/m^3
C^{pc}	Equivalent concentration of concentrate product, keq/m^3
C^{pd}	Equivalent concentration of diluate product, keq/m^3
C_s	Molar concentration of a salt, keq/m^3
C^w	Equivalent concentration of the ED waste stream, keq/m^3
C_x^w	Waste concentration of each contaminate, *x*, keq/m^3
C^y	Concentration difference at any point along the length of the unit, keq/m^3
C^{Δ}	Concentration flux over the entire unit, keq/m^3
E^{des}	Desalination energy, kWh/m^3
E^{pum}	Pumping energy, kWh/m^3
I	Electric current, A
i	Current density, A/m^2
i^{lim}	Limiting current density, A/m^2
i^{prac}	Practically applied current density, A/m^2

K^{cap}	Capital cost, \$/annum
K^{ED}	Total ED cost , \$/annum
K^{op}	Operating cost, \$/annum
L	Length, m
l	Length element in the ED unit, m
Q^{c}	Total flowrate of the concentrate stream, m^3/s
Q^{cr}	Concentrate recycle flowrate, m^3/s
Q^{d}	Total flowrate of the diluate stream, m^3/s
Q^{f}	Total feed into the regenerator, m^3/s
Q^{p}	Total flowrate of the product stream, m^3/s
Q^{r}	Recycle flowrate, m^3/s
Q^{s}	Feed split flowrate, m^3/s
Q^{w}	Total flowrate of the waste stream, m^3/s
r	Recycle ratio
s	Feed split ratio
U	Voltage, V
u	Fluid velocity in electrodialysis unit, m/s
ΔP	Pressure drop, Pa
θ^{d}, θ^{c}	Conductivity constant, Sm^2/keq
κ	Specific conductance, S/m
κ^{av}	Average solution specific conductance, S/m
κ^{d}, κ^{c}	Specific conductance of the diluate or concentrate stream, S/m
κ_x	Specific conductance of contaminant x, S/m
Λ	Solution equivalent conductivity, Sm^2/keq
Λ_x	Equivalent conductivity of contaminant x, Sm^2/keq
π^{d}, π^{c}	Conductivity constant, Sm^2/keq

Integer variable

N	Number of cell pairs

3.3.4 Electrodialysis Design Constraints: Formulation 1

The electrodialysis design was optimised using the global optimisation framework. In the following section, the derivation of the design constraints is presented, followed by the objective function. The derivation of the design equation is based on the single-contaminant design published by Lee et.al (2002).

Equivalent Concentration

As previously described, the concentrations of the solutions in the ED unit are defined according to the equivalent concentration expressions given in Equation (3.1). For the feed, product and waste streams, the equivalent concentration is defined as follows.

$$C^f = \sum_x C_x{}^f \left| z_x v_x \right| \tag{3.8}$$

$$C^p = \sum_x C_x^p \left| z_x v_x \right| \tag{3.9}$$

$$C^w = \sum_x C_x^w \left| z_x v_x \right| \tag{3.10}$$

All subsequent concentrations within the unit are therefore representative of the equivalent concentrations of the mixture of salts.

Electric Current

The degree of desalination across a single stage of the ED unit is known as the concentration flux, C^{Δ}. It is assumed that there is no loss or accumulation of contaminant in the unit, meaning that the amount of contaminant removed from the diluate stream is assumed to equal the total amount taken up by the concentrate stream. Assuming that the diluate and concentrate streams have an equal flowrate, the flux is the change in equivalent concentration of both the concentrate and diluate streams i.e.

$$C^{\Delta} = C^{fd} - C^{pd} = C^{pc} - C^{fc} \tag{3.11}$$

In Equation (3.11), C^{fd} and C^{pd} denote the feed and product concentrations of the diluate stream, while C^{fc} and C^{pc} denote the feed and product concentrations of the concentrate stream. The electrical current is determined using a modified form of Faraday's law. Equation (3.12) relates the driving force with the physical characteristics of the plant, the required capacity and the degree of desalination. Either the cationic or anionic valence and stoichiometric coefficients may be used.

$$I = \frac{FQ^d C^{\Delta}}{N\xi} \sum_x \left| z_x v_x \right| \qquad (3.12)$$

One of the cornerstones of this model is the limiting current density, i^{lim}. Operation of the ED unit is in the ohmic region, meaning that the operating current density cannot exceed the limiting current density. The limiting current density is represented by an empirical equation, Equation (3.13), where φ and σ are experimentally determined constants.

$$i^{lim} = \sigma C^{pd} (u)^{\varphi} \qquad (3.13)$$

This equation assumes uniform flow; in practical applications however, flow is not necessary uniform, and the practically applied current density is reduced. The applied current density, i^{prac}, is expressed as a fraction of i^{lim}, the fraction is known as a safety factor, ε. The resultant expression of the current density is shown in Equation (3.14)

$$i^{prac} = \varepsilon \sigma C^{pd} (u)^{\varphi} \qquad (3.14)$$

Design Considerations

As fluids flow in the diluate compartment, the concentration of salts decreases from the feed concentration, C^{fd}. The concentration at any point in the diluate is known as C^d. Similarly, the concentration in the concentrate is known as C^c, which is higher than the concentrate feed, C^{fc}. The concentration flux at any point, C^y, therefore can be described as:

$$C^y = C^{fd} - C^d = C^c - C^{fc} \qquad (3.15)$$

The cross sectional membrane area is expressed as a product of the membrane width, w, and the differential length, dl, as depicted in Figure 3.3.

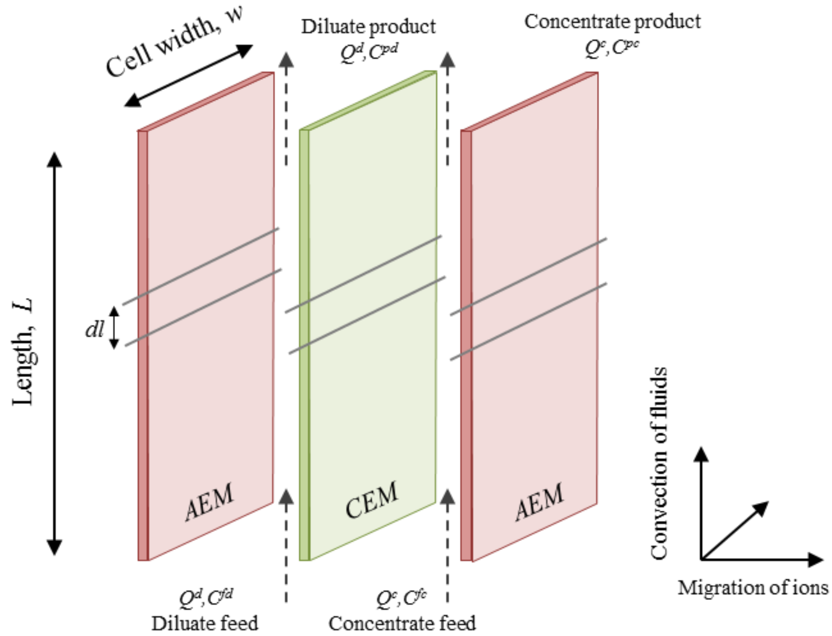

Figure 3.3: Schematic diagram illustrating the direction of fluid flow and ion transfer in a cell pair

The rate of change of flux across a stack is a function of the membrane length, at a constant diluate flowrate, Q^d, the number of cell pairs, N and the current density. This function is given by:

$$dC^y = \frac{iN\zeta}{FQ^d \sum_x z_x v_x} wdl \tag{3.16}$$

In this expression, i represents the current density as it relates to the voltage across the ED unit and solution conductance according to Equation (3.17).

$$i = \frac{\kappa^{av} U}{2\delta N} \tag{3.17}$$

The average specific electrical conductance, κ^{av}, across a single cell pair relates the conductivities of the four constituents of a cell pair according to Equation (3.18). The conductivities of the concentrate and diluate streams are denoted by κ^c and κ^d, while the area resistance of the anion exchange membrane and the cation exchange membrane are ρ^a and ρ^c respectively. The membrane resistances are assumed to be independent of the salts in solution. The average conductivity is given in terms of the distance between any two membranes, i.e. the thickness of the diluate and concentrate cells, δ.

$$\kappa^{av} = \frac{2\delta}{\frac{\delta}{\kappa^c} + \frac{\delta}{\kappa^d} + \rho^a + \rho^c} \quad (3.18)$$

By the combination of Equations (3.16) to (3.18), the rate of change of concentration flux can be given by:

$$dC^y = \frac{U\xi}{FQ^d\left[\frac{\delta}{\kappa^d} + \frac{\delta}{\kappa^c} + \rho^a + \rho^c\right]\sum_x z_x v_x} wdl \quad (3.19)$$

Equation (3.19) provides the basis for calculation of the membrane area and the voltage across the ED stack.

It has been previously established, that the specific conductivity is dependent on the salts in solution and can be related to the concentrations according to Equations (3.2)-(3.6). These relationships can be applied to both the concentrate and diluate streams to determine κ^c and κ^d. For a dilute solution, considering two contaminants, the specific conductivity is:

$$\kappa^d = \sum_{x=1}^{2} a_x^d \Lambda_x C^d (|z_a v_a| + z_c v_c)_x \quad (3.20)$$

Substituting the Deybe-Hückel-Onsager expression, Equation (3.20) becomes:

$$\kappa^d = \sum_{x=1}^{2} a_x^d C^d (|z_a v_a| + z_c v_c)_x \left[\Lambda°_x - (A + B\Lambda°)_x \sqrt{C^d}\right] \quad (3.21)$$

The variable a_x^d represents the molar fractions of salts in the solution. In order to simplify the expression of conductance, two new variables, π^d and θ^d, are defined according to Equations (3.22) and (3.23).

$$\theta^d = \sum_{x=1}^{2} a_x^d (|z_a v_a| + z_c v_c)_x \Lambda°_x \quad (3.22)$$

$$\pi^d = \sum_{x=1}^{2} a_x^d (|z_a v_a| + z_c v_c)_x (A + B\Lambda°)_x \quad (3.23)$$

These can be substituted as coefficients for concentration in the expression for specific conductivity, Equation (3.21), resulting in Equation (3.24).

$$\kappa^d = \theta^d C^d - \pi^d \sqrt{(C^d)^3} \quad (3.24)$$

Similarly, for the concentrate stream, κ^c can be expressed according to Equation (3.25).

$$\kappa^c = \theta^c C^c - \pi^d \sqrt{\left(C^c\right)^3} \tag{3.25}$$

Substituting these expressions for specific conductance into Equation (3.19), the degree of desalination can be expressed as:

$$dC^y = \frac{U\xi}{FQ^d \left[\frac{\delta}{\theta^d C^d - \pi^d \sqrt{\left(C^d\right)^3}} + \frac{\delta}{\theta^c C^c - \pi^c \sqrt{\left(C^c\right)^3}} + \left(\rho^a + \rho^c\right) \right] \sum_x \left| z_x v_x \right|} wdl \tag{3.26}$$

In order to integrate this function, both C^c and C^d must be expressed in terms of C^y. While Equation (3.15) can be used to substitute C^d, it is inadequate for C^c. Due to the recycle streams shown in Figure 3.2, both C^c and C^{fc} cannot be expressed independently of C^y. Based on several runs of an approximation model, it was found that concentrate concentration is linearly dependent on concentration flux, where τ and ω are constant values, i.e.

$$C^c = \tau C^y + \varpi \tag{3.27}$$

Rearranging and substituting Equations (3.15) and (3.27) into (3.26) results in:

$$\frac{1}{\theta_d\left(C^{fd} - C^y\right) - \pi_d \sqrt{\left(C^{fd} - C^y\right)^3}} dC^y + \frac{1}{\theta_c\left(\tau C^y + \varpi\right) - \pi_c \sqrt{\left(\tau C^y + \varpi\right)^3}} dC^y + \frac{\left(\rho^a + \rho^c\right)}{\delta} dC^y = \frac{U\xi}{\delta F Q^d \sum_x \left| z_x v_x \right|} wdl \tag{3.28}$$

Integration of Equation (3.28) along the length of the ED unit with the following boundary conditions results in (3.29) (Wolfram Research, Inc., 2014).

At the inlet of the cell: $C^y = 0$ and $l = 0$.

At the outlet of the cell: $C^y = C^{\Delta}$ as defined in Equation (3.11), and $l = L$.

$$\frac{ln\left|\frac{\left(\theta^{d}-\pi^{d}\sqrt{C^{pd}}\right)\left(\sqrt{C^{fd}}\right)}{\left(\sqrt{C^{pd}}\right)\left(\theta^{d}-\pi^{d}\sqrt{C^{fd}}\right)}\right|}{\theta^{d}}+\frac{ln\left|\frac{\left(\pi^{c}\sqrt{\varpi}-\theta^{c}\right)\left(\sqrt{C^{pc}}\right)}{\left(\pi^{c}\sqrt{C^{pc}}-\theta^{c}\right)\left(\sqrt{\varpi}\right)}\right|}{\tau\theta^{c}}+\frac{\left(\rho^{a}+\rho^{c}\right)}{\delta}C^{\Delta} = \frac{UwL\xi}{\delta FQ^{d}\sum_{x}\left|z_{x}v_{x}\right|} \tag{3.29}$$

The voltage can be related to the current density by Equation (3.17). Substituting Equations (3.24) and (3.25), the voltage expression becomes:

$$U=i^{prac}N\delta\left[\frac{1}{\theta^{d}C^{pd}-\pi^{d}\sqrt{\left(C^{pd}\right)^{3}}}+\frac{1}{\theta^{c}C^{pc}-\pi^{c}\sqrt{\left(C^{pc}\right)^{3}}}+\frac{\left(\rho^{a}+\rho^{c}\right)}{\delta}\right] \tag{3.30}$$

In order to arrive at an expression for the calculation of membrane length, Equation (3.30) is substituted into Equation (3.29). The practical length is therefore given by Equation (3.31).

$$L=\left[\frac{\frac{ln\left|\frac{\left(\theta^{d}-\pi^{d}\sqrt{C^{pd}}\right)\left(\sqrt{C^{fd}}\right)}{\left(\sqrt{C^{pd}}\right)\left(\theta^{d}-\pi^{d}\sqrt{C^{fd}}\right)}\right|}{\theta^{d}}+\frac{ln\left|\frac{\left(\pi^{c}\sqrt{\varpi}-\theta^{c}\right)\left(\sqrt{C^{pc}}\right)}{\left(\pi^{c}\sqrt{C^{pc}}-\theta^{c}\right)\left(\sqrt{\varpi}\right)}\right|}{\tau\theta^{c}}+\frac{\left(\rho^{a}+\rho^{c}\right)}{\delta}C^{\Delta}}{i^{prac}N\delta\left[\frac{1}{\theta^{d}C^{pd}-\pi^{d}\sqrt{\left(C^{pd}\right)^{3}}}+\frac{1}{\theta^{c}C^{pc}-\pi^{c}\sqrt{\left(C^{pc}\right)^{3}}}+\frac{\left(\rho^{a}+\rho^{c}\right)}{\delta}\right]}\right]\times\left[\frac{FQ^{d}}{w\xi}\sum_{x}\left|z_{x}v_{x}\right|\right] \tag{3.31}$$

Spacers are features of an ED unit that provide structural integrity as well as promote uniform flow. These spacers result in the decrease of the theoretical volumetric flowrate; this is accounted for by introducing a correction factor, α. To minimise the pressure difference across the membranes, it is assumed that the concentrate and diluate streams have equal flowrates, i.e. $Q^d = Q^c$. The volumetric flowrate is therefore given by Equation (3.32).

$$Q^{c}=Q^{d}=Nw\delta u\alpha \tag{3.32}$$

Based on the geometry of the concentrate and diluate cells, the total required area is determined as a function of the practical length and the width of the cell, i.e.

$$A = \frac{2LwN}{\beta} \tag{3.33}$$

The spacers also have an effect of reducing the area available for current to traverse the unit. In order to counteract this shadow effect, a factor, β, is introduced, such that the practically applied area is larger than the theoretically calculated area.

Energy requirements

The total energy consumption considered in an electrodialysis unit can be attributed to the migration of electrons across the membranes as well as the energy required to pump the solutions through the unit.

i. *Desalination Energy*

The energy required for desalination is determined based on the voltage across the ED stack, according to Equation (3.30) and the current, described by Equation (3.12). Using ohms law, the amount of energy thus required to desalinate contaminated water is given by:

$$E^{des} = \frac{UI}{Q^p} \tag{3.34}$$

ii. *Pumping Energy*

The pumping energy required is largely dependent on the pressure drop across the ED unit. The spacers in the ED cell promote mixing and generate turbulence in the fluid, however, the fluid velocity is low enough for the flow to be considered laminar. As such, the pressure drop across the unit can be expressed using the following relationship (Nikonenko et al., 1999).

$$\Delta P = -\frac{12\mu u L}{\delta^2} \tag{3.35}$$

Equation (3.35) is a modified Hagen-Poiseille expression, based on flow of a fluid in a thin rectangular slit, as is the case in the diluate and concentrate compartments in the ED unit. Subsequently, the energy required for pumping can be described as follows, the where η is the pumping efficiency and k^{tr} is a conversion factor.

$$E^{pum} = \frac{k^{tr}}{\eta}|\Delta P| \tag{3.36}$$

Material Balances

Material balances around each of the mixing and splitting junctions are necessary to ensure conservation of mass and connectivity with the greater water network. Based on Figure 3.2, the following material balances apply:

$$Q^f = Q^p + Q^w \tag{3.37}$$

$$Q^f = Q^d + Q^s \tag{3.38}$$

$$Q^d = Q^p + Q^r \tag{3.39}$$

$$Q^c = Q^s + Q^{cr} \tag{3.40}$$

$$Q^w = Q^c + Q^r - Q^{cr} \tag{3.41}$$

The recovery rate, *r,* is the amount of diluate that is recovered as product. It is related to the amount of diluate that is recycled and mixed with the concentrate stream, in order to reduce its salinity. The purpose or this is to minimise osmotic transport across the membranes. The purged concentrate is then replaced by an amount of the less concentrated feed, according to the split ratio, *s*.

$$r = \frac{Q^p}{Q^d} \tag{3.42}$$

$$s = \frac{Q^d}{Q^f} \tag{3.43}$$

For the mixing points on Figure 3.2, load balances are also required. All concentrations refer to the equivalent concentration of the overall solution as previously defined. It is noteworthy that for a single stage model, $C^{pd} = C^p$, and $C^f = C^{fd}$.

$$Q^f C^{fd} = Q^p C^p + Q^w C^w \tag{3.44}$$

$$Q^{c}C^{fc} = Q^{s}C^{fd} + Q^{cr}C^{cr} \tag{3.45}$$

$$Q^{w}C^{w} = Q^{c}C^{pc} + Q^{r}C^{p} - Q^{cr}C^{cr} \tag{3.46}$$

Finally, an overall mass balance around the entire ED stack is conducted

$$Q^{d}C^{fd} + Q^{c}C^{fc} = Q^{c}C^{c} + Q^{d}C^{d} \tag{3.47}$$

Objective Function

The objective function is expressed as a cost function; this enables one to simultaneously minimized both the size of the unit and the energy consumption. These are expressed as the capital and operating costs as follows:

i. Capital costs

The determining factor in the capital cost estimation of an ED unit is the size and quantity of membranes required, i.e. the stack area, A.

$$K^{cap} = A^{f}k^{mb}A \tag{3.48}$$

The capital cost is annualised according to an estimate of the membrane life span using an annualisation factor, A^f, is used to account for depreciation. This factor is given by Equation (3.49) (Chew et al., 2008; Khor et al., 2011).

$$A^{f} = \left(\frac{m(1+m)^{t}}{(1+m)^{t} - 1^{t}} \right) \tag{3.49}$$

ii. Operating costs

Operating costs are due to energy consumption for pumping and desalination purposes.

$$K^{op} = t^{d}k^{el}Q^{p}\left(E^{des} + E^{pum}\right) \tag{3.50}$$

The overall objective function of the electrodialysis unit is derived by combining the capital and operating costs.

$$K^{ED} = A^{f} k^{mb} A + t^{d} k^{el} Q^{p} \left(E^{des} + E^{pum} \right) \quad (3.51)$$

The total costs to be minimised are given by Equation (3.51) subject to constraints given in Equations (3.8) to (3.14) and (3.30) to (3.47).

3.3.5 Electrodialysis Design Constraints: Formulation 2

The formulation presented in Section 3.3.4 is specific to a binary mixture of simple salts. If the model is to be applied to other salts, the concentration-conductivity relationship may have to be adjusted and many of the constraints would no longer hold. As the number and complexity of the electrolytes increases, the derivation and integration would become increasingly complex. This would be mathematically and computationally expensive. For this reason, an alternate formulation is proposed.

The basis of this alternative formulation is that the equivalent conductivity is assumed to be constant over the entire unit. Similar to Lee et al. (2002), the conductance is assumed to be linearly dependent on the concentration, according to Equation (3.52).

$$\kappa_i = \Lambda C_i \qquad (3.52)$$

However, in this work, instead of assuming a constant fixed value for the conductivity, Λ, the equivalent conductivity is calculated based on the concentration of the contaminants in the feed solution to the ED unit. Lee et al. (2002) conducted an experiment that proved that for a 600% change in concentration, there is only a 10% variation in conductivity. It is therefore assumed that the concentration flux over the unit is sufficiently small such that the change in conductivity is negligible. Therefore, for salts where the conductivity displays a similarly weak dependence on concentration, this alternate formulation can be adopted.

The derivation of the constraints follows a similar progression as described in Section 3.3.4. The relevant constraints are summarized in the following paragraphs.

The equivalent concentrations of the feed, product and final concentrate (waste) streams are as follows:

$$C^f = \sum_x C_x{}^f \left| z_x v_x \right| \tag{3.53}$$

$$C^p = \sum_x C_x^p \left| z_x v_x \right| \tag{3.54}$$

$$C^w = \sum_x C_x^w \left| z_x v_x \right| \tag{3.55}$$

The electric current and current density display the same relationships, as the concentration flux is dependent on the stoichiometric coefficients and valence of all contaminants.

$$I = \frac{FQ^d C^{\Delta}}{N\xi} \sum_x \left| z_x v_x \right| \tag{3.56}$$

$$i^{prac} = \varepsilon\sigma C^d (u)^{\varphi} \tag{3.57}$$

The degree of desalination is related to the rate of change of area by Equation (3.58).

$$dC^y = \frac{U\xi}{FQ^d \left[\frac{\delta}{\kappa^d} + \frac{\delta}{\kappa^c} + \rho^a + \rho^c \right] \sum_x \left| z_x v_x \right|} wdl \tag{3.58}$$

In this case however, the specific conductance is related to the concentration by Equation (3.52). Once again, considering a binary mixture of simple salts, the conductivity of the system, Λ, is given by Equations (3.59)-(3.62). In these expressions, the feed stream was used as a basis for the calculation of system conductivity (Anderko and Lencka, 1997; Strathmann, 2004c; Wright, 2007).

$$\Lambda_x = \Lambda_x{}^{\circ} - (A + B\Lambda_x{}^{\circ})\sqrt{C_x^f} \qquad \forall x \in X \tag{3.59}$$

$$\Lambda_x = \frac{\kappa_x}{C_x^f \left(z_{cat} v_{cat} + z_{an} v_{an} \right)} \qquad \forall x \in X \tag{3.60}$$

$$\kappa = \sum_x a_x \kappa_x \tag{3.61}$$

$$\Lambda = \frac{\kappa}{\sum_x C_x{}^f \left(z_{cat}v_{cat} + z_{an}v_{an}\right)_x} \tag{3.62}$$

Subsequently, the following expression is derived for the rate of change of flux:

$$dC^y = \frac{U\zeta w}{FQ^d\left[\dfrac{\delta}{\Lambda C^c} + \dfrac{\delta}{\Lambda C^d}\rho^a + \rho^c\right]\sum_x |z_x v_x|} dl \tag{3.63}$$

Based on Equation (3.16), the limiting current density is related to the voltage by Equation (3.64).

$$i^{prac} = \frac{U}{N\delta\left[\dfrac{1}{\Lambda C^d} + \dfrac{1}{\Lambda C^c} + \dfrac{\left(\rho^a + \rho^c\right)}{\delta}\right]} \tag{3.64}$$

Substituting Equation (3.64) into (3.63) followed by integration between the following boundary conditions results in Equation (3.65) for the calculation of length.

At the inlet of the cell: $C^y = 0$ and $l = 0$.

At the outlet of the cell: $C^y = C^\Delta$ and $l = L$.

$$L = \frac{\left[ln\dfrac{C^{pc}C^{fd}}{C^{pd}C^{fc}} + \dfrac{\left(\rho^a + \rho^c\right)\Lambda C^\Delta}{\delta}\right]C^{pd}FQ^d}{\left[\dfrac{C^{pd}}{C^{pc}} + 1 + \dfrac{\Lambda C^{pd}}{\delta}\left(\rho^a + \rho^c\right)\right]i^{prac}\xi}\sum_x |z_x v_x| \tag{3.65}$$

The volumetric flowrate and total area are defined as follows:

$$Q^d = Nw\delta v\alpha \tag{3.66}$$

$$A = \frac{2LwN}{\beta} \tag{3.67}$$

The voltage across the entire ED unit is given by Equation (3.68)

$$U = \left[\frac{ln\frac{C^{pc}C^{fd}}{C^{pd}C^{fc}}}{\Lambda C^\Delta} + \left(\rho^a + \rho^c\right)\right]\frac{C^\Delta NFQ^d}{wL\zeta}\sum_x z_x v_x \tag{3.68}$$

The calculation of desalination and pumping energy follow the same procedure as in the previous formulation i.e. Equations (3.69) to (3.71).

$$E^{des} = \frac{UI}{Q^p} \tag{3.69}$$

$$\Delta P = -\frac{12\mu v L}{\delta^2} \tag{3.70}$$

$$E^{pum} = \frac{k^{tr}}{\eta}\left|\Delta P\right| \tag{3.71}$$

The material balance expressions for this formulation are also based on the schematic representation given in Figure 3.2. The following Equations (3.72) to (3.83) apply:

$$Q^f = Q^p + Q^w \tag{3.72}$$

$$Q^f = Q^d + Q^s \tag{3.73}$$

$$Q^d = Q^p + Q^r \tag{3.74}$$

$$Q^c = Q^s + Q^{cr} \tag{3.75}$$

$$Q^w = Q^c + Q^r - Q^{cr} \tag{3.76}$$

$$r = \frac{Q^p}{Q^d} \tag{3.77}$$

$$s = \frac{Q^d}{Q^f} \tag{3.78}$$

$$Q^f C^{fd} = Q^p C^p + Q^w C^w \tag{3.79}$$

$$Q^c C^{fc} = Q^s C^{fd} + Q^{cr} C^{cr} \tag{3.80}$$

$$Q^w C^w = Q^c C^{pc} + Q^r C^p - Q^{cr} C^{cr} \tag{3.81}$$

$$C^{\Delta} = C^{fd} - C^d = C^c - C^{fc} \tag{3.82}$$

$$Q^d C^{fd} + Q^c C^{fc} = Q^c C^c + Q^d C^d \tag{3.83}$$

The objective function, combining the capital expenditure and operating costs, is given by Equation (3.84).

$$K_{ED} = A^f k^{mb} A + t^d k^{el} Q^p \left(E^{des} + E^{pum} \right) \qquad (3.84)$$

The objective is minimised subject to constraints given in Equations (3.53) to (3.57), (3.59) to (3.62) and (3.65) to (3.83).

3.4 Integrated Water Network Optimisation Model

The water network superstructure, given in Figure 3.4 provides the basis for the development of the WNS model. It shows all possible source-sink, source-regenerator, regenerator-sink connections. Based on this, the optimal structure can be selected. The model consists primarily of material balances expressions and logical constraints. The nonlinear electrodialysis model developed in Section 3.3 is embedded into the model to represent the regeneration unit.

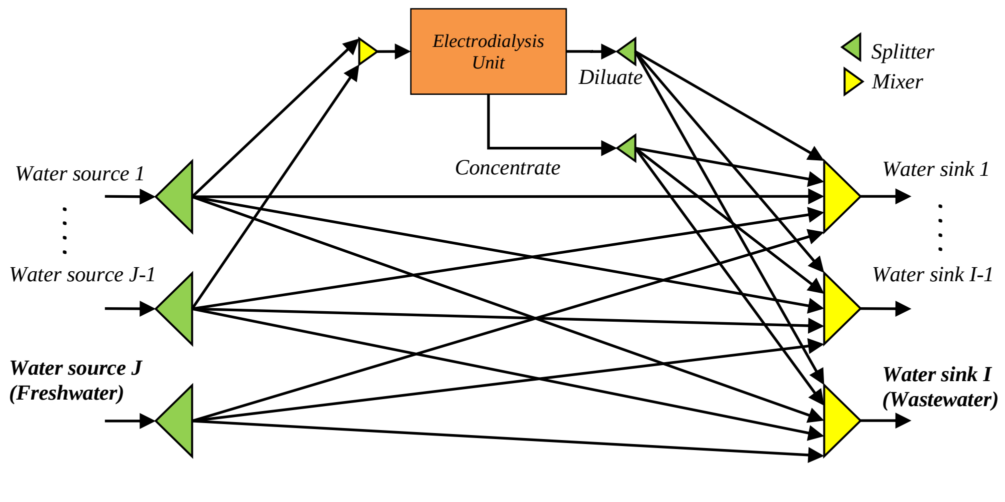

Figure 3.4: Superstructure representation of the water network

A fixed flowrate approach was taken in the model development, i.e. a stream is described by the total flowrate of fluid and the concentration of each of the contaminants in the stream. This approach was selected due to its suitability for complex problems, its ability to be integrated with non-mass transfer water treatment units, compatibility with mathematical modelling techniques (as described in Section 2.3.4.

3.4.1 Problem Statement

The problem can be stated as follows. Given:

(i) A set of water sinks, I, with known flowrates, F_i, and known maximum allowable concentrations, $C_{i,x}^U$;

(ii) A set of water sources, J, with known flowrates, F_j, and known contaminant concentrations, $C_{j,x}$;

(iii) A single regenerator, i.e. electrodialysis unit, with some design operating and costing parameters;

(iv) A freshwater source, with a variable flowrate and known contaminant concentrations; and

(v) A wastewater sink, with a variable flowrate and known maximum allowable contaminant concentrations.

It is required to determine:

(i) The water network that minimises the amount of freshwater consumed, wastewater produced, the energy consumed in the regeneration unit and the overall cost of the water network; and

(ii) The optimum operating and design conditions of the electrodialysis unit (e.g. area, number of cell pairs, current and voltage).

3.4.2 Assumptions

In developing a mathematical model for the water network, the following assumptions are made:

i. The number of water-using and water treating operations are fixed;
ii. The water flowrates, and subsequently the total flowrates, through all water-using processes are fixed (this excludes the freshwater source and the final wastewaters sink);
iii. The influence of thermal and pressure effects on the mixing and splitting of sources and sinks is negligible;
iv. The freshwater is contaminant-free and cannot be fed to the regenerator;
v. The concentration flux across the ED unit is sufficiently small that the conductivity can be assumed constant over the unit i.e. Formulation 2 given in Subsection 3.3.5 can be used;
vi. Linear blending is assumed at all mixing nodes and treatment units; and
vii. All assumptions listed in Subsections 3.3.2 for the electrodialysis unit apply.

3.4.3 Water Network Nomenclature

Below is a list of the parameters and variables used in the development of water network optimisation model and the embedded electrodialysis model.

Sets

J	$\{j\|j$ is a water source$\}$
I	$\{i\|i$ is a water sink$\}$
X	$\{x\|x$ is an ionic contaminant$\}$

Water Network Parameters

$C_{j,x}$	Concentration of contaminant, x, in source, j
$C_{n,x}{}^{U}$	Maximum allowable concentration for contaminant, x, in sink, i
$D_{j,i}$	Manhattan distance between source, j, and sink, i
$D_i^{r,con}$	Manhattan distance between regenerator (concentrate) and sink i
$D_i^{r,dil}$	Manhattan distance between regenerator (diluate) and sink i
$D^r{}_j$	Manhattan distance between source j and regenerator
F_j	Total flowrate from source j, m^3/s
F^L	Minimum feasible flowrate in pipes, m^3/s
F_i	Total flowrate into sink i, m^3/s
k^{FW}	Cost of freshwater, \$/m^3
k^{WW}	Cost of wastewater treatment, \$/m^3
m	Interest rate
p	CEPCI constant
q	CEPCI constant
u^p	Pipe linear velocity, m/s
t	Pipe life span, years

Electrodialysis Design Parameters

A,B	Equivalent conductivity constants
F	Faradays constant, As/keq
k^{el}	Cost of electricity, \$/kWh
k^{mb}	Cost of membrane, \$/m^2

k^{tr}	Conversion factor, MJ/kWh
liq	Liquid recovery for regenerator
RR_x	Removal ratio of contaminant x in regenerator
t	Maximum lifespan of ED unit and plant, years
t^d	Total operating days of ED, s/annum
v^c, v^a	Stoichiometric coefficient of a cation or anion
w	Membrane width, m
z^c, z^a	Valence of a cation or anion
z_x	Cationic or anionic valence of salt x
α	Shadow factor
β	Volume factor
δ	Cell thickness, m
ε	Safety factor
ζ	Current utilization
η	Pumping efficiency
$\Lambda°$	Infinite equivalent conductivity, Sm^2/keq
μ	Fluid viscosity, kg/sm
v_x	Stoichiometric coefficient of salt x
$\rho^c+\rho^a$	Total resistance of cation exchange and anion exchange membranes, Ωm^2
σ	Limiting current density constant, As^bm^{1-b}/keq
φ	Limiting current density constant

Water Network Variables

$F_{j,i}$	Total flowrate from source, j to sink, i, m^3/s
F^r_j	Total flowrate from source, j to regenerator, m^3/s
$F_i^{r,con}$	Total flowrate from concentrate stream in regenerator, r, to sink i, m^3/s
$F_i^{r,dil}$	Total flowrate from diluate stream in regenerator, r, to sink i, m^3/s
FW_i	Total flowrate from freshwater source to sink, i, m^3/s
WW_j	Total flowrate from source, j, to wastewater sink, m^3/s

ED Design Variables

A	Total unit area, m^2
C^c	Equivalent concentration at any point in the concentrate stream, keq/m^3
C^{cr}	Equivalent concentration of concentrate recycle, keq/m^3
C^d	Equivalent concentration at any point in the diluate stream, keq/m^3
C_{eq}	Equivalent concentration of salts in ED unit, keq/m^3
C^f	Equivalent concentration of the ED feed, keq/m^3
C^{fc}	Equivalent concentration of concentrate feed, keq/m^3
C^{fd}	Equivalent concentration of diluate feed, keq/m^3
C^p	Equivalent concentration of the ED product stream, keq/m^3
C^{pc}	Equivalent concentration of concentrate product, keq/m^3
C^{pd}	Equivalent concentration of diluate product, keq/m^3
C_s	Molar concentration of a salt, keq/m^3
C^w	Equivalent concentration of the ED waste stream, keq/m^3
C_x^w	Waste concentration of each contaminate, x, keq/m^3
C^y	Concentration difference at any point along the length of the unit, keq/m^3
C^{Δ}	Concentration flux over the entire unit, keq/m^3
E^{des}	Desalination energy, kWh/m^3
E^{pum}	Pumping energy, kWh/m^3
I	Electric current, A
i	Current density, A/m^2
i^{lim}	Limiting current density, A/m^2
i^{prac}	Practically applied current density, A/m^2
K^{cap}	Capital cost, \$/annum
K^{ED}	Total ED cost , \$/annum
K^{op}	Operating cost, \$/annum
L	Length, m
l	Length element in the ED unit, m
Q^c	Total flowrate of the concentrate stream, m^3/s

Q^{cr}	Concentrate recycle flowrate, m^3/s
Q^d	Total flowrate of the diluate stream, m^3/s
Q^f	Total feed into the regenerator, m^3/s
Q^p	Total flowrate of the product stream, m^3/s
Q^r	Recycle flowrate, m^3/s
Q^s	Feed split flowrate, m^3/s
Q^w	Total flowrate of the waste stream, m^3/s
r	Recycle ratio
s	Feed split ratio
U	Voltage, V
u	Fluid velocity in electrodialysis unit, m/s
ΔP	Pressure drop, Pa
θ^d, θ^c	Conductivity constant, Sm^2/keq
κ	Specific conductance, S/m
κ^{av}	Average solution specific conductance, S/m
κ^d, κ^c	Specific conductance of the diluate or concentrate stream, S/m
κ_x	Specific conductance of contaminant x, S/m
Λ	Solution equivalent conductivity, Sm^2/keq
Λ_x	Equivalent conductivity of contaminant x, Sm^2/keq
π^d, π^c	Conductivity constant, Sm^2/keq

Integer Variables

N	Number of cell pairs

Binary Variables

$$Y_{j,i} \quad \begin{cases} 1 \leftarrow & \text{Interconnecting stream between source } j \text{ and sink } i \text{ exists} \\ 0 \leftarrow & \text{Otherwise} \end{cases}$$

Y^r_j $\begin{cases} 1 \leftarrow & \text{Interconnecting stream between source } j \text{ and regenerator feed exists} \\ 0 \leftarrow & \text{Otherwise} \end{cases}$

$Y_i^{r,con}$ $\begin{cases} 1 \leftarrow & \text{Interconnecting stream between regenerator concentrate and sink } i \text{ exists} \\ 0 \leftarrow & \text{Otherwise} \end{cases}$

$Y_i^{r,dil}$ $\begin{cases} 1 \leftarrow & \text{Interconnecting stream between regenerator diluate and sink } i \text{ exists} \\ 0 \leftarrow & \text{Otherwise} \end{cases}$

Y^r $\begin{cases} 1 \leftarrow & \text{Regenerator exists} \\ 0 \leftarrow & \text{Otherwise} \end{cases}$

3.4.4 Water Network Constraints

The material balance constraints described in the following section follow the source-regenerator-sink formulation commonly used in water network synthesis and optimisation (Chew et al., 2008; Khor et al., 2012b, 2011).

Material Balance Constraints

i. Water Balances for Sources

A material balance is conducted around the splitter that follows each source, *j*. Each water source has the potential to be split into multiple streams for reuse/recycle in the sinks, regeneration in the ED unit or sent to the wastewater sink, as described by Equation (3.85).

$$F_j = \sum_i F_{j,i} + F_j^r \qquad \forall\ j \in J \qquad (3.85)$$

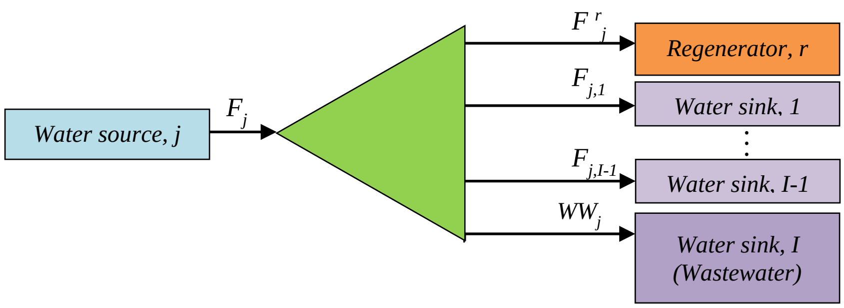

Figure 3.5: Mass balance around each water source splitter

While it is possible to express the effluent sink as a separate entity, in this work it was represented as one of the water sinks. A water sink, as described in Section 2.3.4, is a water using process that demands or consumes a certain flowrate of water. The effluent stream meets this definition, as water is fed to the stream for final treatment. The waste sink is differentiated from other water using operations by the fact that its flowrate, WW_j, is variable. If effluent is assumed to flow to the final sink, the following definition applies.

$$WW_j = F_{j,i} \qquad \forall\ i = |I| \qquad (3.86)$$

ii. Water Balances for Sinks

Similarly, a material balance is conducted around the mixers feeding into each water sink. As represented in Figure 3.6, the flow requirements of each sink are potentially satisfied by all the water sources, including freshwater, and the concentrate and diluate streams from the regenerator; this relationship is given in Equation (3.87).

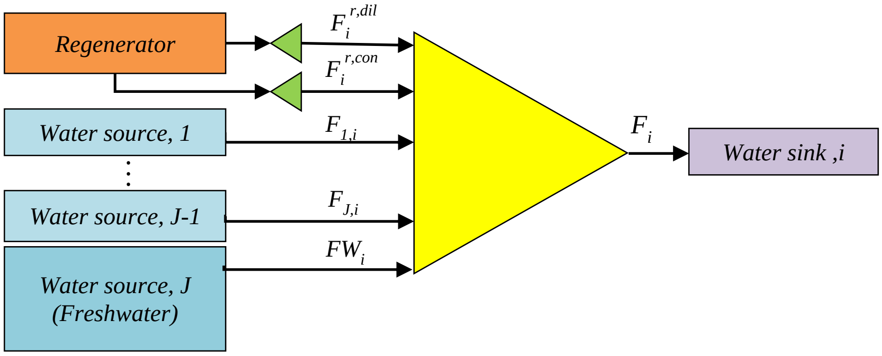

Figure 3.6: Mass balance around pre-sink mixers

$$F_i = \sum_j F_{j,i} + F_i^{r,dil} + F_i^{r,con} \qquad \forall\, i \in I \qquad (3.87)$$

Similar to the wastewater sink, the freshwater stream can be expressed as a water source, with a variable flowrate. The freshwater term need not be stated explicitly in Equation (3.87), provided that it is defined separately:

$$FW_i = F_{j,i} \qquad \forall\ j = |J| \qquad (3.88)$$

A corresponding contaminant balance is conducted, for each contaminant. Equation (3.89) is expressed and an inequality implying that that the total concentration of a given contaminant in a sink cannot exceed the maximum allowable concentration, $C^U_{i,x}$.

$$C^U_{i,x} \geq \frac{\sum_j C_{j,x} F_{j,i} + F_i^{r,dil} C_x^{r,dil} + F_i^{r,con} C_x^{r,con}}{F_i} \qquad \forall i \in I; x \in X \qquad (3.89)$$

iii. Water Balances for Water Treatment Units

Figure 3.7 shows a schematic diagram of a simplified regeneration unit. The corresponding total water and contaminant material balances are given in Equation (3.90) and. (3.91), respectively.

$$\sum_j F_j = \sum_i F_i^{r,dil} + \sum_i F_i^{r,con} \qquad (3.90)$$

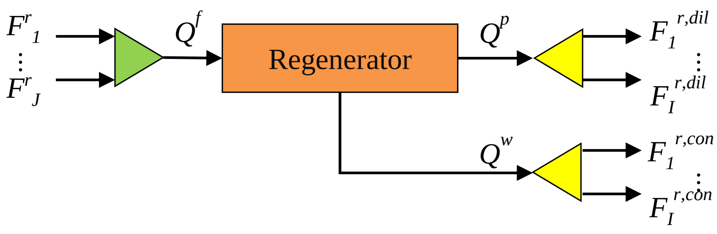

Figure 3.7: Schematic diagram depicting material balance around the regeneration unit

$$\sum_j C_{j,x} F_j = C_x^{r,dil} \sum_i F_i^{r,dil} + C_x^{r,con} \sum_i F_i^{r,con} \qquad \forall\ x \in X \qquad (3.91)$$

For ease of integration with the nonlinear regeneration model, it is necessary to determine the total amount of water flowing into and out of the regeneration units, as such; the following definitions must be introduced.

$$Q^f = \sum_j F_j^r \qquad (3.92)$$

$$Q^p = \sum_i F_i^{r,dil} \qquad (3.93)$$

$$Q^w = \sum_i F_i^{r,con} \qquad (3.94)$$

A corresponding load balance is performed to determine the amount of each contaminant in the streams around the regeneration unit.

$$Q^f C_x^f = \sum_j F_j^r C_{j,x}^r \qquad \forall\ x \in X \qquad (3.95)$$

$$C_x^p = C_x^{r,dil} \qquad \forall\ x \in X \qquad (3.96)$$

$$C_x^w = C_x^{r,con} \qquad \forall\ x \in X \qquad (3.97)$$

iv. Regenerator Performance Expressions

Removal ratio refers to the mass load of contaminant exiting in the concentrate stream of a regenerator as a fraction of the feed. It is given by the following expression:

$$RR_x = \frac{C_x^{r,con} \sum_i F_i^{r,con}}{\sum_j C_{j,x} F_j^r} \qquad \forall\ x \in X \qquad (3.98)$$

The liquid recovery expresses the fraction of water fed into the unit that is recovered to the diluate stream of the regenerator. It is given by the following expression:

$$liq = \frac{Q^p}{Q^f} \qquad (3.99)$$

In cases where the black box approach is adopted, the Equations (3.98) and (3.99) would be sufficient in the representation of the regeneration unit. For a fixed removal ratio, in a black box model, the regeneration model would be linear, which is favourable for modelling purposes. As an alternative to the black box approach, a more accurate detailed model of a treatment unit can be used. This will be described in the following section.

Electrodialysis Constraints

For an accurate representation of regeneration costs, the detailed ED model developed in Section 3.3 is embedded into the WNS model. The simplified electrodialysis formulation, referred to as *Formulation 2* is adopted. The detailed derivation of these expressions is given from Pages 3-95 to 3-99; the relevant constraints are summarized below. Firstly the equivalent concentrations of feed and output streams are determined using the equivalent concentration definition (Strathmann, 2004b)

$$C^f = \sum_x C_x^f \left| z_x v_x \right| \qquad (3.100)$$

$$C^p = \sum_x C_x^p \left| z_x v_x \right| \qquad (3.101)$$

$$C^w = \sum_x C_x^w \left| z_x v_x \right| \qquad (3.102)$$

The conductivity of each contaminant is calculated using Equation (3.103), based on the feed concentration. These are the used to determine the overall solution specific conductance, κ, and equivalent conductivity, Λ.

$$\Lambda_x = \Lambda_x{^\circ} - (A + B\Lambda_x{^\circ})\sqrt{C_x^f} \qquad \forall x \in X \qquad (3.103)$$

$$\kappa = \sum_x a_x \Lambda_x C_x^f \left(z_{cat} v_{cat} + z_{an} v_{an} \right)_x \qquad (3.104)$$

$$\Lambda = \frac{\kappa}{\sum_x C_x^f \left(z_{cat} v_{cat} + z_{an} v_{an} \right)_x} \qquad (3.105)$$

The electric current, area, voltage and energy are calculated as follows:

$$I = \frac{FQ^d C^\Delta}{N\xi} \sum_x z_x v_x \qquad (3.106)$$

$$i^{prac} = \varepsilon \sigma C^d (u)^\varphi \qquad (3.107)$$

$$L = \frac{\left[ln \frac{C^{pc} C^{fd}}{C^{pd} C^{fc}} + \frac{\left(\rho^a + \rho^c\right) \Lambda C^\Delta}{\delta} \right] C^{pd} F Q^d}{\left[\frac{C^{pd}}{C^{pc}} + 1 + \frac{\Lambda C^{pd}}{\delta} \left(\rho^a + \rho^c\right) \right] i^{prac} \xi} \sum_x \left| z_x v_x \right| \qquad (3.108)$$

$$U = \left[\frac{ln \frac{C^{pc}C^{fd}}{C^{pd}C^{fc}}}{\Lambda C^{\Delta}} + \left(\rho^{a} + \rho^{c}\right) \right] \frac{C^{\Delta} NFQ^{d}}{wL\zeta} \sum_{x} \left| z_{x} v_{x} \right| \tag{3.109}$$

$$Q^{d} = Nw\delta v\alpha \tag{3.110}$$

$$A = \frac{2LwN}{\beta} \tag{3.111}$$

$$E^{des} = \frac{UI}{Q^{p}} \tag{3.112}$$

$$E^{pum} = \frac{k^{tr}}{\eta} \left| -\frac{12\mu vL}{\delta^{2}} \right| \tag{3.113}$$

The material balances are based on the schematic layout shown in Figure 3.2. The ED unit is related to the superstructure by Equations (3.92) to (3.97). Within the unit, water and load balances are given by Equations (3.114) to (3.124).

$$Q^{f} = Q^{d} + Q^{s} \tag{3.114}$$

$$Q^{d} = Q^{p} + Q^{r} \tag{3.115}$$

$$Q^{c} = Q^{s} + Q^{cr} \tag{3.116}$$

$$Q^{w} = Q^{c} + Q^{r} - Q^{cr} \tag{3.117}$$

$$Q^{f} C^{fd} = Q^{p} C^{p} + Q^{w} C^{w} \tag{3.118}$$

$$Q^{c} C^{fc} = Q^{s} C^{fd} + Q^{cr} C^{cr} \tag{3.119}$$

$$Q^{w} C^{w} = Q^{c} C^{pc} + Q^{r} C^{p} - Q^{cr} C^{cr} \tag{3.120}$$

$$C^{\Delta} = C^{fd} - C^{d} = C^{c} - C^{fc} \tag{3.121}$$

$$Q^{d} C^{fd} + Q^{c} C^{fc} = Q^{c} C^{c} + Q^{d} C^{d} \tag{3.122}$$

$$r = \frac{Q^{p}}{Q^{d}} \tag{3.123}$$

$$s = \frac{Q^{d}}{Q^{f}} \tag{3.124}$$

Logical Constraints

Additional constraints are included to govern the existence of interconnections between the units, prevent the existence of unnecessary streams and treatment units and to minimise complexity of the model. These constraints involve the introduction of binary variables.

i. Flowrate Upper and Lower Bounds

It is common practice to impose an arbitrarily large value as the maximum flowrate of interconnecting streams, with a corresponding minimum of zero. However, this potentially results in an unnecessarily large search space. This can be overcome by the introduction of hard bounds. These constraints are based on insights gained following topological network analysis (Meyer and Floudas, 2006; Misener and Floudas, 2010). For example, the flowrates of the streams emerging from any one source are limited by the total flowrate of that particular source. The minimum flowrate, F^L represents the lowest physically feasible flowrate that can be achieved in the pipe.

$$F^L Y_{j,i} \le F_{j,i} \le Y_{j,i} F_j \qquad \forall\ j \in J ; i \in I \qquad (3.125)$$

$$F^L Y_j^r \le F_j^r \le Y_j^r F_j \qquad \forall\ j \in J \qquad (3.126)$$

$$F^L Y_i^{r,dil} \le F_i^{r,dil} \le Y_i^{r,dil} \sum_j F_j \qquad \forall\ i \in I \qquad (3.127)$$

$$F^L Y_i^{r,con} \le F_i^{r,con} \le Y_i^{r,con} \sum_j F_j \qquad \forall\ i \in I \qquad (3.128)$$

Hard bounds may also be necessary to govern the existence of the regeneration unit i.e. if the feed to the regenerator is very small, treatment unit will not exist as the resulting plant size would be impractical.

$$F^L Y^r \le Q^f \le Y^r \sum_j F_j \qquad (3.129)$$

ii. Prevention of Remixing

The binary variables are introduced to prevent remixing of the diluate and concentrate streams from the regenerator in a particular sink.

$$Y_i^{r,dil} + Y_i^{r,con} \leq 1 \qquad \forall\ i \in I \qquad (3.130)$$

Objective Function

The water network and electrodialysis model culminate in an overall cost function to be minimised, given by Equation (3.131). All pipes are assumed to operate at the same fluid velocity, u^p, and use the same costing coefficients *p* and *q*. the piping cost is calculated as a function of the Manhattan distance, D , between any two units.

$$\min \left(\begin{array}{l} k^{FW} \sum_{i \in I} FW_i + k^{WW} \sum_{j \in J} WW_j + A^f k^{mb} A + t^d k^{el} Q^p \left(E^{des} + E^{pum} \right) \\ + A^f \left[\begin{array}{l} \sum_{j \in J} \sum_{i \in I} D_{j,i} \left(\dfrac{pF_{j,i}}{3600 u^p} + qY_{j,i} \right) + \sum_{j \in J} D_i^r \left(\dfrac{pF_j^r}{3600 u^p} + qY_j^r \right) + \\ \sum_{i \in I} D_i^{r,dil} \left(\dfrac{pF_i^{r,dil}}{3600 u^p} + qY_i^{r,dil} \right) + \sum_{i \in I} D_i^{r,con} \left(\dfrac{pF_i^{r,con}}{3600 u^p} + qY_i^{r,con} \right) \end{array} \right] \end{array} \right) \qquad (3.131)$$

The cost of piping and the ED capital cost are annualised using a factor that accounts for depreciation of the equipment over its usable life span, *t*. This annualisation factor A^f is given by Equation (3.49) (Chew et al., 2008; Khor et al., 2011).

The objective function, Equation (3.131), is minimised subject to constraints given in Equations (3.85) to (3.130).

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4

MODEL APPLICATION

4.1 Introduction

In this chapter, using case studies presented in the literature, applicability of the developed models is demonstrated. The first investigation is a comparison between the two alternative formulations of the standalone electrodialysis models. In the subsequent sections, using a pulp and paper case study, several scenarios of the WNS are presented. Firstly, the WNS with a detailed ED regenerator model is compared to a black box WNS model. Secondly, based on the detailed model, a comparison is given between regenerator models with fixed and variable removal ratios. Finally, for the variable removal ratio case, a comparison is given between direct global optimisation and the use of a sequential solution approach.

4.2 Electrodialysis Design Model

The standalone electrodialysis models developed in Section 3.3 of Chapter 3 were applied to a paper mill case study. The aim was to design an ED unit for the purpose of chloride removal as would be seen in a typical Kraft paper mill plant. The same case study was used for the exact model (Formulation 1) and the simplified design model (Formulation 2) and the results for the two were compared.

4.2.1 Case Study

A case study was based on the data given by Pfromm (1997). In this process, the electrostatic precipitator (ESP) dust, comprising mainly of sodium sulphate, was dissolved and passed through the ED unit. It was necessary to dechlorinate the ESP dust suspension before recycling it to the black liquor. A schematic diagram of this process is shown in Figure 4.1. The ESP dust contains 1250 kg/day of sodium chloride (NaCl) and 13900 kg/day of sodium sulphate ($NaSO_4$); water is added to this mixture to make up the feed to the electrodialysis unit.

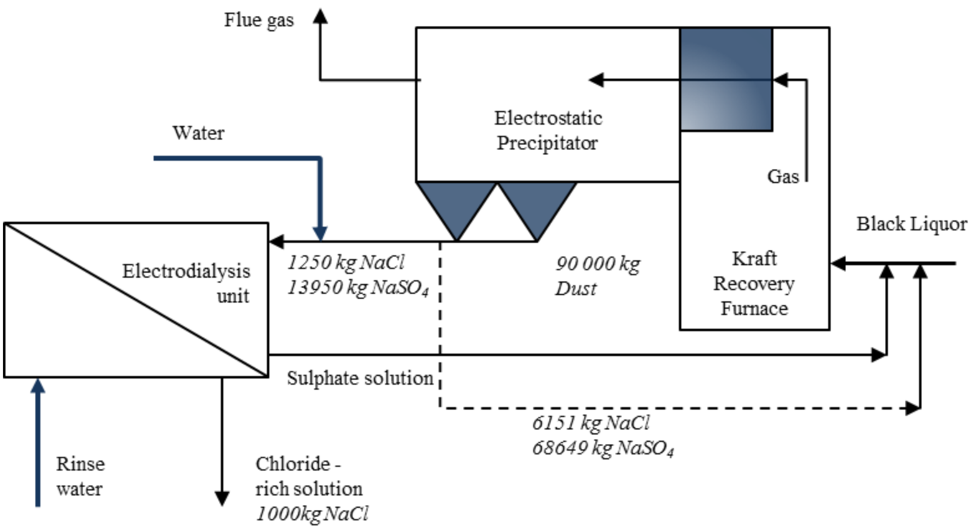


Figure 4.1: Application of electrodialysis for chloride removal in the Kraft process, showing average daily flows (Pfromm, 1997)

It was required to design an ED unit that would reduce the NaCl to 250 kg/day in the sulphate-rich solution, which is recycled to the black liquor. This corresponds to a removal ratio of 90%

The parameters used in the case study are based on typical ED units used in the Kraft process and in the desalination of brine. Table 4.1 gives the parameters relating to the plant specifications (Pfromm, 1997; Rapp and Pfromm, 1998b).

Table 4.1: Plant Design Specifications

	Parameter		Value
Q^f	Plant capacity, m^3/s		0.0012
t^d	Annual operation, days/annum		330
t	Plant life span, years		5
m	Interest rate, %		5
		NaCl	$NaSO_4$
C_x^f	Feed Concentrations, keq/m^3	0.2057	0.9443
C_x^p	Product Concentrations, keq/m^3	0.0459	0.9474

The membrane resistance and empirical constants for limiting current density were assumed to take the same values as those used for the desalination of brine (Tsiakis and Papageorgiou, 2005). Table 4.2 shows the input parameters used for the comparison.

Table 4.2: Input Parameters for ED design

	Parameter		Value
α	Volume factor		0.8
β	Shadow factor		0.7
ε	Safety factor		0.7
σ	Limiting current density constant, $As^{b}m^{1-b}/keq$		25 000
φ	Limiting current density constant		0.5
η	Pumping efficiency		0.7
w	Cell width, m		0.42
ζ	Current utilization		0.9
$\rho^{c}+\rho^{a}$	Total resistance of membranes, Ωm^2		0.0007
		NaCl	$NaSO_4$
$\Lambda_x°$	Infinite conductivity (Haynes, 2014)	126.39	129.80

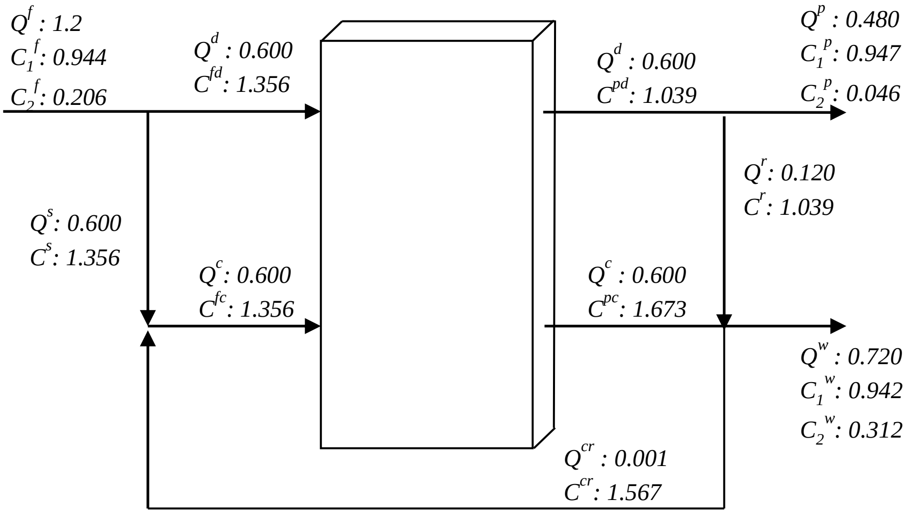
4.2.2 Results

Table 4.3 shows the relevant design variables that would result in minimal ED cost with respect to both operating and capital costs. A comparison was conducted between the exact model and the simplified formulation. Deviations of up to 3% were observed in the key operating conditions and design variables resulting from the two formulations. This is considered a reasonable margin of error for a detailed design and cost estimate (Sinnott, 2009).

Table 4.3: Comparison of variables from the exact model and the simplified formulation

	Formulation 1	**Formulation 2**	**Δ**
Current, A	125.1	125.1	0%
Limiting current density	1727.6	1727.5	0%
Total area, m^2	43.8	42.6	-3%
Length, m	0.19	0.18	-3%
Voltage, V	151.4	156.3	+3%
Cell pairs	275	275	0%
Energy consumption, kWh/m^3	11.0	11.3	+3%
Pressure drop, Pa	53.1	51.4	+3%
Fluid velocity, m/s	0.1	0.1	0%
Total cost, $/annum	19314.2	19961.0	+3%

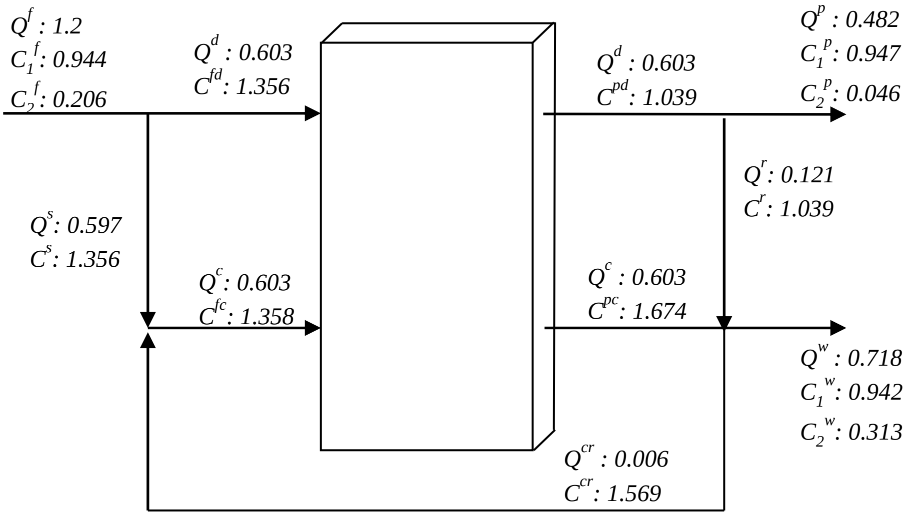
Figure 4.2 shows the flowrates and concentrations for all the streams around the ED unit using the exact model, i.e. Formulation 1. For the individual concentrations in the feed and product streams, subscript 1 refers to sodium sulphate and subscript 2 refers to sodium chloride. For the intermediate streams, equivalent concentrations are given.



*flowrates in dm^3/s, concentrations in keq/m^3

Figure 4.2: Resultant flowsheet showing optimal flowrates and concentrations around the ED unit using Formulations 1

Similar results are given for the model using Formulation 2, in Figure 4.3. A comparison between the two flowsheets shows that the material balances around each of the units results in similar flowrates. The most noticeable difference is that in the second formulation, a larger flowrate is recycled from the waste stream to the concentrate feed, Q^{cr}. This is possibly due to the shorter unit length in the second formulations, which resulted in higher diluate and concentrate flowrates, and therefore a larger recycle stream.



**flowrates in dm^3/s, concentrations in keq/m^3*

Figure 4.3: Resultant flowsheet showing optimal flowrates and concentrations around the ED unit using Formulation 2

4.2.3 Solution Procedure and Model Characteristics

Both formulations resulted in MINLP problems. A sequential approach was taken, by first relaxing the integer constraint, i.e. solving an RMINLP, and using this solution to initialise the MINLP problem. The models were solved using a combination of DICOT and BARON solvers in GAMS® (Tawarmalani and Sahinidis, 2005). Model characteristics for both formulations are summarized in Table 4.4.

Table 4.4: Comparison of model characteristics from the exact model and the simplified formulation

	Formulation 1	**Formulation 2**
Solver – RMINLP	BARON	BARON
Solver – MINLP	DICOPT	DICOPT
Continuous variables	49	53
Integer variables	1	1
Computational time, s	16	3
Tolerance	0.00001	0.00001

4.2.4 Discussion

The ED model is highly nonlinear, as it involves logarithmic, bilinear and exponential terms. BARON was valuable in linearizing these constraints and producing a non-integer solution for the RMINLP that was globally optimal, within the set tolerance. This provided a very good starting point for the solution of the MINLP solution using DICOPT. Using a single solver or for the MINLP directly would increase the computational time significantly. In this case study, the computational resources required to optimise both models were minimal. The exact model took 16 CPU seconds to solve while the simplified model took only 3 CPU seconds. However, it can be expected that if the exact model is embedded into a larger optimisation model, e.g. within a water network, the computational expense will increase. In such scenarios, the simplified formulation is advantageous.

Formulation 1 provided the derivation of the exact solution but it was mathematically intensive. The simplification of the model that assumed a single, non-constant value for equivalent conductivity resulted in a similar unit design. Formulation 2 can therefore reliably be used with background processes. The development of the exact model requires derivation that is specifically for a binary mixture of simple electrolytes. It is not easily adapted for complex salts, or for ternary mixtures. Formulation 2, on the other hand, is easily adaptable. It is only necessary to employ the appropriate conductivity-concentration relationship and mixing expression. Furthermore, in order to increase reliability of the model, when a strong conductivity-concentration dependence is observed, it is advised that the exact formulation is adopted.

Based on the similarity of the unit designs and flowrates, the exact model and simplified models can reliable be used interchangeably with reasonable confidence in the results. The selection between Formulations 1 and 2 would depend on the whether the design is a standalone model or it is combined with a background process, as well as the nature and complexity of the feed mixture.

4.3 Integrated Water Network Optimisation Model

The WNS model developed in Section 3.4 of Chapter 3, hereafter referred to as the detailed model, was applied to a pulp mill and bleached paper plant adapted from Chew et al. (2008). This case study was used to draw comparison between the utility requirements when using a detailed model and the black box model.

4.3.1 Case Study

In the original scenario, shown in Figure 4.4, four separate freshwater feeds are used, with a total consumption of 8 500 tonnes per day, and 4 separate effluent streams are produced, totalling 10 500 tonnes per day.

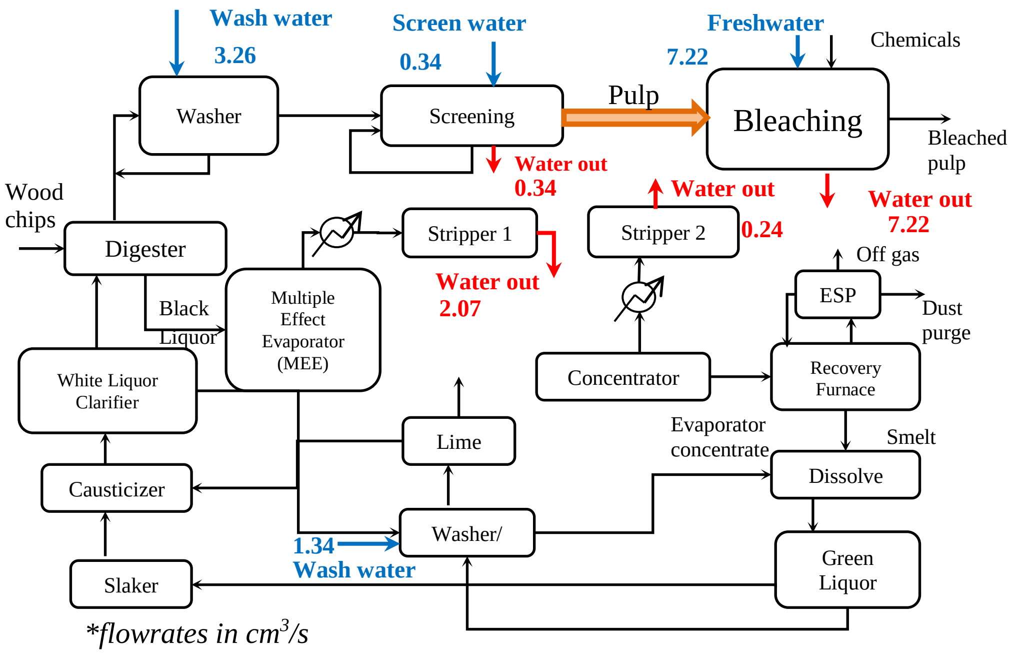


Figure 4.4: Simplified PDF of Pulp mill and bleached paper plant (Chew et al., 2008)

Two contaminants were identified, namely, NaCl and $MgCl_2$. The flowrates and contaminant concentrations of the sources and sinks are detailed in Table 4.5.

Table 4.5: Input data for water network

Sources				Sinks			
Source	Flowrate (cm^3/s)	Concentration (keq/cm^3) NaCl	$MgCl_2$	Sink	Flowrate (cm^3/s)	Maximum Concentration (keq/cm^3) NaCl	$MgCl_2$
Stripper 1	2.07	0	0	Washer	3.26	0.0046	0.0004
Screening	0.34	0.046	0.035	Screening	0.34	0.0125	0.0007
Stripper 2	0.24	0	0	Washer/filter	1.34	0	0
Bleaching	7.22	0.026	0.0002	Bleaching	7.22	0.0002	0.00003
Freshwater	Variable	-	-	Wastewater	Variable	0.01	0.01

The costing parameters used in the WNS and ED design are given in Table 4.6 (Khor et al., 2011; Tsiakis and Papageorgiou, 2005). A constant Manhattan distance of 100 m and pipe velocity of 1 m/s were assumed (Chew et al., 2008). Based on the case study, the minimum flowrate, F^{min}, was assigned a value of 0.001 cm^3/s. Relevant input parameters for the ED unit are given in Table 4.7.

Table 4.6: WNS costing parameters

	Parameter	Value
k^{el}	Unit cost of electricity, \$/kwH	0.12
k^{mb}	ED membrane cost, \$/m^2	150
k^{ww}	Freshwater unit cost, \$/m^3	1
k^{fw}	Wastewater treatment unit cost, \$/m^3	1
m	Interest rate, %	5
t	Estimated plant life span, years	5
t^d	Annual operating time, days	330
q	Pipe costing parameter (carbon steel)	250
p	Pipe costing parameter (carbon steel)	7200

Table 4.7: Input parameters for ED design

	Parameter		Value
α	Volume factor		0.8
β	Shadow factor		0.7
ε	Safety factor		0.7
σ	Limiting current density constant		25 000
φ	Limiting current density constant		0.5
η	Pumping efficiency		0.7
w	Cell width, m		0.42
ζ	Current utilization		0.9
$\rho^a+\rho^c$	Total resistance of membranes, Ωm^2		0.0007
F	Faraday constant, As/keq		96 500 000
		NaCl	**$MgCl_2$**
$\Lambda_x°$	Infinite conductivity (Haynes, 2014)	126.39	129.34
RR	Removal ratio	90%	60%

4.3.2 Solution Procedure

Two process integration scenarios were compared. Input parameters, including removal ratio, for the ED unit were kept constant for comparison between the two cases.

Scenario 1: Water minimisation only using a black box approach for WNS, i.e. Equations (3.100) to (3.124) were omitted from the formulation. The results from the WNS were then input to a standalone ED model in order to determine the true cost of regeneration under those conditions. The cost of regeneration for the black box model was estimated based on a linear expression, as is common practice in black box optimisation (Chew et al., 2008; Tan et al., 2009). The costing parameter for ED was independently calculated based on a standalone ED model. The ED cost was determined based solely on the throughput. This solution procedure is outlined in Figure 4.5 (a).

Scenario 2: Simultaneous water and energy minimisation using the detailed model. The ED design was performed as part of the WNS using the model formulation described in Section 3.4.4. This procedure is outlined in Figure 4.5 (b).

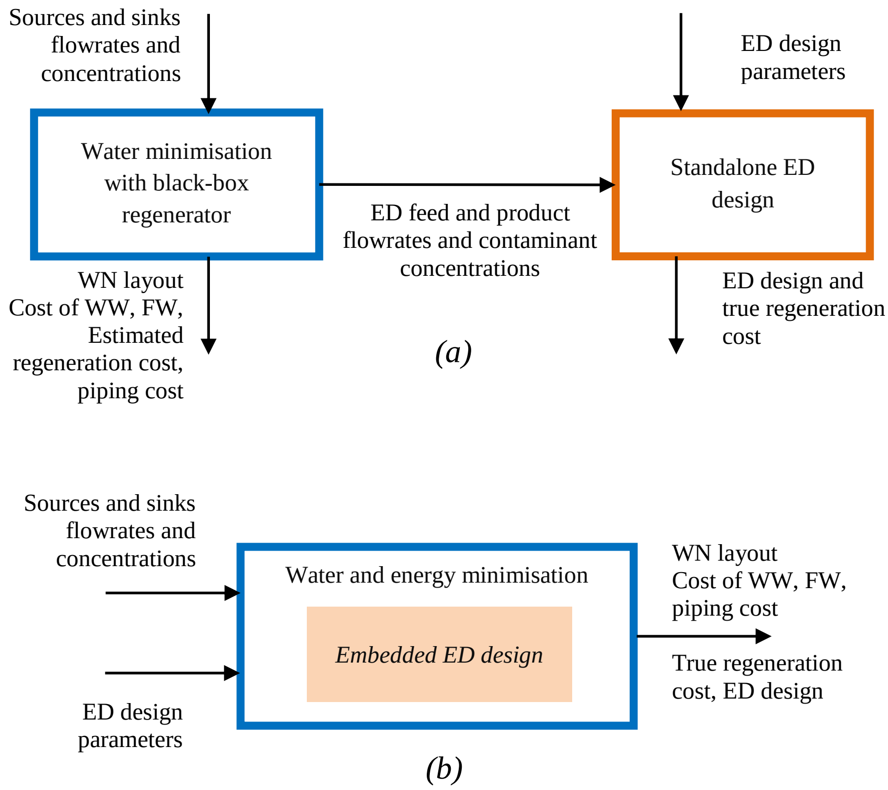


Figure 4.5: Flowchart representing the solution procedures followed in (a) Scenario 1 and (b) Scenario 2, showing model inputs and outputs

4.3.3 Results

Table 4.8 shows the major cost factors determined by the optimisation model for the base case and each of the two modelling scenarios. These factors include the purchasing cost of freshwater, treatment cost of wastewater, regeneration cost, which comprises capital and operating cost, and the cost of cross plant piping. For Scenario 1, the ED cost is given first based on the linear cost function (estimated ED cost) and the accurate cost of ED using the black box inputs (true ED cost).

Table 4.8: Resultant water network cost factors for Scenarios 1 and 2

	Base Case	**Scenario 1**		**Scenario 2**
	Original	Estimated ED cost	True ED cost	
Freshwater	2 814.86	1 776.00	1 776.00	1 736.70
Wastewater	3 468.12	1 122.80	1 122.80	1 083.50
Regeneration	-	3.90	26.08	5.22
Piping	-	92.40	92.40	86.62
Total cost	6 282.98	2 995.10	3 017.28	2 912.07

** Costs are given in $K/annum*

Scenario 1: Water Minimisation

In this scenario, the objective was water minimisation. The resultant flowsheet after process integration is given in Figure 4.6. Simple water minimisation results in a 37% saving in freshwater and 68% reduction in wastewater generated, compared to the original plant. Table 4.8 shows that there is an 85% discrepancy between the regeneration cost as determined by the linear cost function ($3.90K/annum) and the cost of the actual required ED unit under the same conditions ($26.08K/annum). Overall, the water minimisation model resulted in 52% reduction in the total cost of the water network.

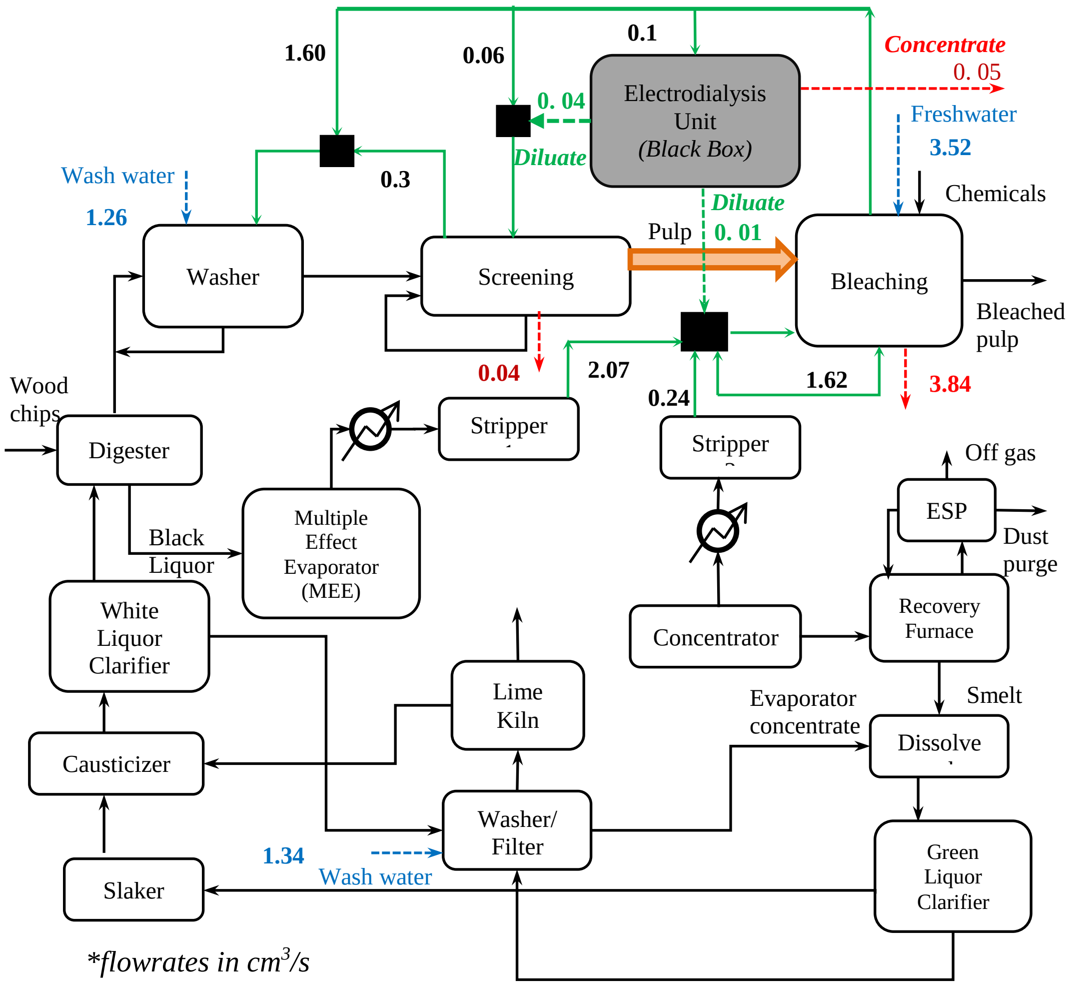


Figure 4.6: Pulp and paper plant following water minimisation, showing new cross plant piping connections

Scenario 2: Water and Energy Minimisation

In comparison with the base case, process integration resulted in a 38% reduction in freshwater consumption and 69% reduction in the production of wastewater. After accounting for the cost treatment and piping, this resulted in a 54% decrease in the total cost of the water network, from $6.2M/annum to $2.9M/annum. The final plant configuration after process integration is shown in Figure 4.7.

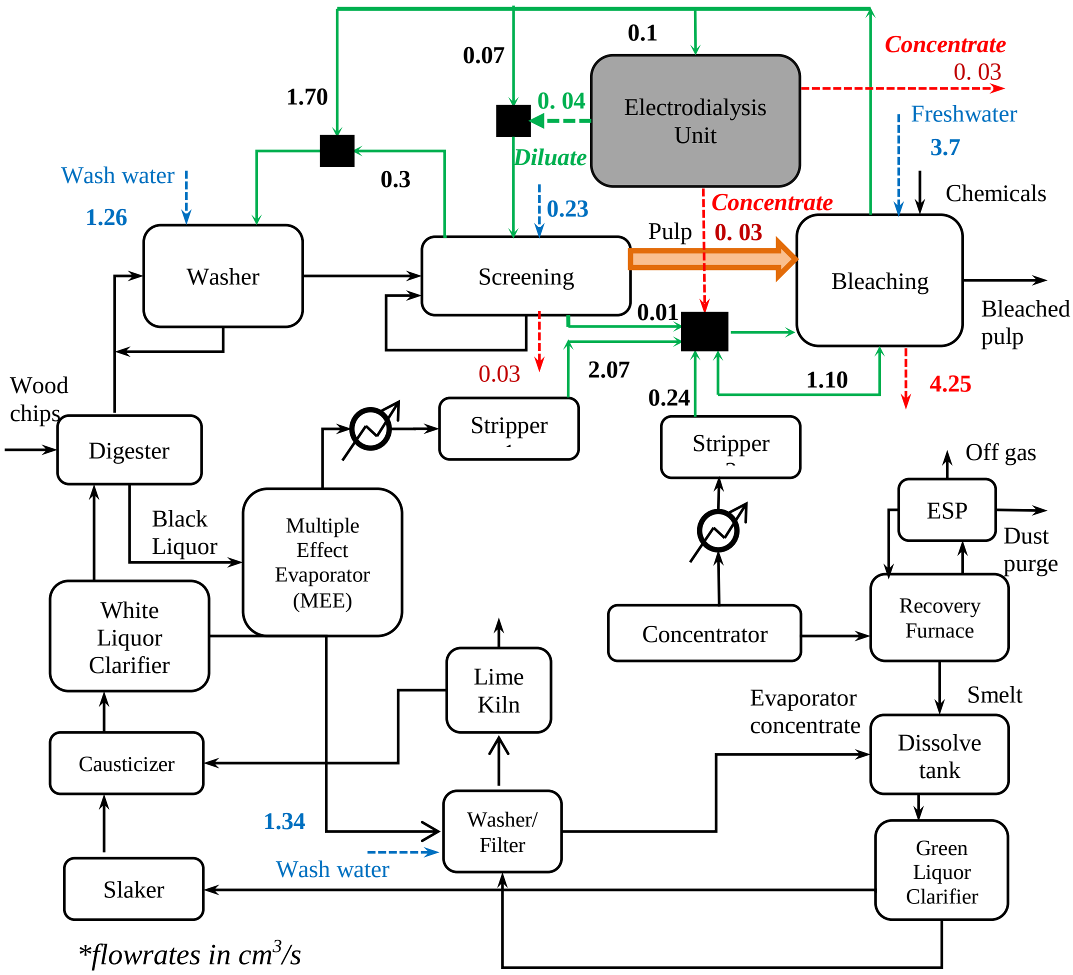


Figure 4.7: Pulp and paper plant following water and energy minimisation, showing new cross plant piping connections

From a comparison between Figure 4.6 and Figure 4.7, it can be observed that plant configurations attained in the first and second scenarios are similar, with regards to the interconnections. The main difference lies in the total flowrates of freshwater and wastewater to and from the system. The total freshwater and wastewater treatment requirements decreased from Scenario 1 to Scenario 2.

From Table 4.8, a 6.2% decrease in the cost of cross-plant piping is also observed, from $92.4K in Scenario 1 to $86.62K in Scenario 2. Most significantly, an 80% decrease is observed between the actual cost of regeneration in the water minimisation scenario ($26.08K/annum) and the cost of regeneration in Scenario 2 ($5.22K/annum). This can be attributed to the fact that when the optimisation of the ED is embedded into the water network, the required unit has a more conservative design and consumes 98% less energy. Table 4.9 shows key electrodialysis variables determined in the optimisation, highlighting the difference between the two scenarios.

Table 4.9: Comparison between key design characteristics of the ED unit in Scenarios 1 and 2

	Unit	**Scenario 1**	**Scenario 2**	**Δ**
Area	m^2	438	144	-67%
Number of cell pairs		353	229	-35%
Desalination energy	kWh/annum	105 494	18 476	-98%
Pumping energy	kWh/annum	912.3	18.32	-98%
Total cost	$/annum	26 083	5 216	-80%

4.3.4 Model Characteristics

In both cases, the MINLP was solved directly, using BARON (Tawarmalani and Sahinidis, 2005). The key characteristics of the models are presented and compared in Table 4.10. While the model sizes are similar, the time taken to solve the integrated model (Scenario 2) was close to 21 hours, while the black box (Scenario 1) required only 2 minutes. This is attributed to the increased complexity of the highly nonlinear detailed model.

Table 4.10: Summary of model characteristics for Scenarios 1 and 2

	Scenario 1	**Scenario 2**
Solver	BARON	BARON
Continuous variables	125	145
Integer variables	41	42
Computational time, s	115	75 565
Tolerance	0.001	0.001

4.3.5 Discussion

The black box model, on its own, presents the risk of misrepresenting the water network and gives no insight into the required ED unit. When coupled with a standalone regenerator design model, the linear cost function largely underestimates the cost of treatment. The linear cost function considers only the flowrate of feed to the ED while the true cost is determined by all aspects of the design, leading to an 85% discrepancy as shown in Table 4.8. By simultaneously designing the ED unit within the water network, all aspects of the regeneration requirements are factored into the plant design. This also has the effect of potentially reducing the overall utility requirement.

In this particular case study, the integrated model resulted in a 98% reduction in the actual energy consumption, including both pumping and desalination energy. The reason why the change is so drastic is due to the fact that ED is electrically driven. As a result, by optimising the throughput, feed concentrations and design variables, the required driving force, i.e. electricity can be reduced. This translated to an 80% decrease in the overall cost of retrofitting the ED unit.

However, the combination of the nonlinear ED model and the nonconvex WNS model increases the complexity of the overall model, thus increasing the computational requirement. The sequential approach adopted for the standalone ED model (Section.4.2) was found to be unsuccessful in this case. Due to the presence of binary variables, a branch and bound approach was most favourable, and so BARON was used directly.

It is evident from the results that the black box approach has the potential of reporting a suboptimal solution with regards to the water network and the ED design. However, the marginal improvement in optimality gained by the detailed simultaneous design comes at the significant expense of along computational time. This trade off, between accuracy and computational time exists in many modelling problems. The choice of the black box model would be favourable in cases where high accuracy is not of upmost importance, for example, in order of magnitude estimates or plant design for preliminary economic evaluation studies. However, for detailed plant design, accuracy is important and the integrated approach is advisable.

4.4 Removal Ratio Comparison

It was identified that the WNS problem can potentially be further improved by varying the regenerator performance. As such, an investigation was done in order to observe the impact of removal ratio in the formulation. The same case study described in Section 4.3 was used, introducing a third scenario.

Scenario 3: Energy and water minimisation with a variable removal ratio for both contaminants in the ED unit. All other conditions were kept constant (i.e. the same as Scenario 2). A comparison was then drawn between Scenario 2 (fixed removal ratio) and Scenario 3 (variable removal ratio).

4.4.1 Results

The results for Scenario 3 are given in Table 4.11, together with the values obtained in the base case and in Scenario 2 for comparison. When compared to the base case, Scenario 3 resulted in a 38% reduction in freshwater consumption from $2.8M/annum to $M1.7/annum. The corresponding reduction in wastewater treatment cost is 68% which decreased from $3.4M/annum in the base case to $1.1M/annum in Scenario 3. The overall cost savings as a result of process integration according to Scenario 3 is 55%.

Table 4.11: Resultant water network cost factors for Scenarios 2 and 3

	Base Case	**Scenario 2**	**Scenario 3**
Freshwater	2 814.86	1 736.70	1 739.23
Wastewater	3 468.12	1 083.50	1 083.46
Regeneration	-	5.22	2.85
Piping	-	86.62	63.89
Total cost	6 282.98	2 912.04	2 889.43

* *Costs are given in $K/annum*

Comparing the detailed models with fixed removal ratios (Scenario 2) to the case with variable removal ratios (Scenario 3) there was very little improvement in the freshwater consumption and wastewater production. The overall cost of the water network reduced from $2.91M/annum in Scenario 2 to $2.89M/annum in Scenario 3. More significantly, the regeneration cost decreased from $5.22K/annum in Scenario 2 to $2.85K/annum in Scenario 3, corresponding to a 45% decrease. The removal ratios in Scenario 2 were fixed at 90% and 60% for NaCl and $MgCl_2$ respectively. However, in Scenario 3, optimum values were found to be 76% for NaCl and 80% for $MgCl_2$. The key design variables for the ED units obtained in each scenario are given in Table 4.12.

Table 4.12: Comparison between key design characteristics of the ED unit in Scenarios 2 and 3

		Unit	Scenario 2	Scenario 3	Δ
Removal ratio:	NaCl		0.90	0.76	-16%
	$MgCl_2$		0.60	0.80	+33%
Area		m^2	144	67	-53%
Number of cell pairs			229	107	-53%
Desalination energy		kWh/annum	18 476	17 164	-7%
Pumping energy		kWh/annum	18.32	28.51	+56%
Total ED cost		$/annum	5 216	2 847	-45%

By varying the removal ratio, the required membrane area reduced from 144 m^2 to 67 m^2, while the number of cell pairs reduced from 229 to 107. This corresponded with a 7 % decrease in the desalination energy. The pumping energy increased by 56% due to the fact that the throughput remained unchanged while the unit size decreased.

The resultant flowsheet is given in Figure 4.8. When compared with the fixed removal ratio case, Figure 4.7, it can be observed that the flowsheet is significantly modified. Different and fewer interconnections are selected in

Scenario 3. For this reason, the cost of piping decreased from \$86K/annum in Scenario 2 to \$64K/annum in Scenario 3.

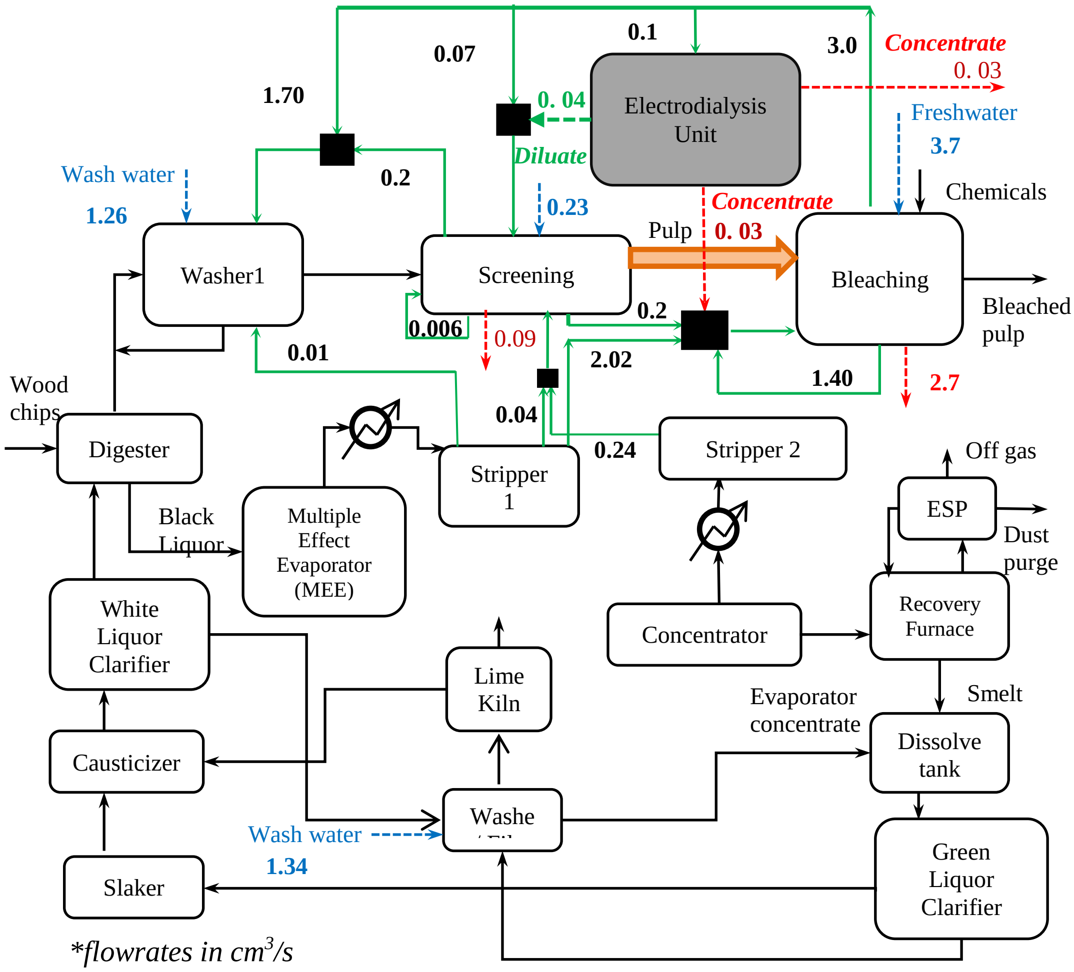


Figure 4.8: Pulp and paper plant following water and energy minimisation with a variable contaminant removal ratio, showing new cross plant piping connections

4.4.2 Model Characteristics

For comparison, BARON was used as a direct global optimisation solver in both Scenario 2 and Scenario 3. The increase in the number of variables corresponds with the addition of RR_x for each contaminant. The computational time required increased from 21 hours to over 55 hours. The tolerance was reduced in Scenario 3 to speed up convergence.

Table 4.13: Summary of model characteristics for Scenarios 2 and 3

	Scenario 2	**Scenario 3**
Solver	BARON	BARON
Continuous variables	145	147
Integer variables	42	42
Computational time, s	75 565	199 459
Tolerance	0.001	0.01

4.4.3 Discussion

By allowing the removal ratio to vary, the degree of contaminant removal in the ED unit was specific to the requirement of the water network under consideration. This avoids the unnecessary expense of energy that is achieved by removing more contaminant than necessary. This is seen in the case where removal ratio for NaCl decreased from 90% in Scenario 2 to 76% in Scenario 3. Concurrently, the degree of removal of $MgCl_2$ increased from 60% to 80%. This indicates that was a potential for further removal of $MgCl_2$ without compromising on energy consumption. In order to fully exploit the trade-off between contaminant removal (i.e. freshwater minimisation) and energy consumption, it is necessary to allow the removal ratio to vary.

By specifying the removal ratio, in Scenario 2, the feasible region was constrained. Varying the removal ratio introduced additional degrees of freedom to the model and increased the size of the feasible region. Consequently, the computational time increased significantly. The removal ratio is considered a complicating variable, as it partakes in a bilinear expression (refer to Equation 3.94). As a result, allowing the removal ratio to vary increases the nonconvexity of the model, adding to computational requirements. This is evidenced by the 62% increase in CPU time observed.

Freshwater consumption and wastewater production were not largely affected by the variation of removal ratio. While the cost of regeneration decreased by 45%, the overall water network cost only decreased by 1%. From design perspective, it is more accurate to allow removal ratio to vary. The consequences of fixing the removal ratio are the overdesign of regeneration units and the introduction of potentially avoidable stream interconnections. This may become more important in cases where multiple regenerators are considered.

4.5 Sequential Solution Procedure for WNS Problems

In the previous section it was established that the variability of removal ratio in the WNS model is critical for optimum design. However this comes at the expense of a high computational time when using direct global optimisation. A fourth scenario was proposed to determine if a sequential procedure could be used to achieve similar results.

Scenario 4. Energy and water minimisation with a detailed ED model. All conditions were kept constant (i.e. the same as Scenario 2 and 3). A sequential solution procedure according to Figure 4.9 was employed.

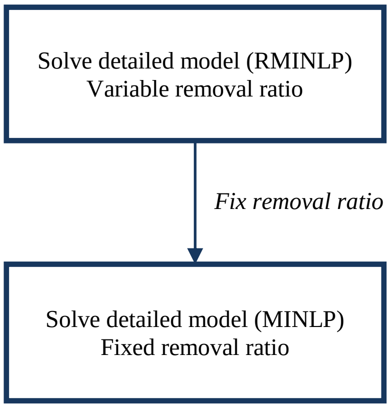


Figure 4.9: Sequential algorithm for the solution of integrated WNS

A comparison was then drawn between Scenario 3 (direct solution procedure) and Scenario 4 (sequential solution procedure).

4.5.1 Results

Table 4.14 shows the comparison between the base case, the best solution (Scenario 3) and the results obtained by the sequential approach shown in Figure 4.9. Scenario 4 resulted in a 2% increase in wastewater production and no change in freshwater consumption, in comparison with Scenario 3. The sequential procedure also resulted in an increase in the cost of regeneration, from \$2.85K/annum in Scenario 3 to \$2.95K/annum in Scenario 4. This corresponds to a 4% increase. The cost of piping decreased by 43%.

Table 4.14: Resultant water network cost factors for Scenarios 3 and 4

	Base Case	**Scenario 3**	**Scenario4**
Freshwater	2 814.86	1 739.23	1 739.23
Wastewater	3 468.12	1 083.46	1 111.97
Regeneration	-	2.85	2.95
Piping	-	63.89	36.16
Total cost	6 282.98	2 889.42	2 890.31

* *Costs are given in \$K/annum*

The electrodialysis unit designed as a result if the sequential solution procedure had an area of 62 m2; 7% less than the area obtained in Scenario 3. The total energy requirement increased from 17 MWh/annum in Scenario 3 to 22MWh/annum in Scenario 4. This comparison is presented in Table 4.15.

Table 4.15: Comparison between key design characteristics of the ED unit in Scenarios 3 and 4

	Unit	Scenario 3	Scenario 4	Δ
Removal ratio:	NaCl	0.76	0.75	-2%
	$MgCl_2$	0.80	0.80	0%
Area	m^2	67	62	-7%
Number of cell pairs		107	106	-1%
Length	m	0.75	0.7	-7%
Desalination energy	kWh/annum	17 164	22 410	+31%
Pumping energy	kWh/annum	28.51	28.51	0%
Total ED cost	$/annum	2 847	2 947	+7%

4.5.2 Model Characteristics

BARON was used as the solver for both the RMINLP and the MINLP in Scenario 4. The cumulative computational time was 14 hours, 75% less than the time required in the direct global optimisation model.

Table 4.16: Summary of model characteristics for Scenarios 3 and 4

	Scenario 3	Scenario 4
Solver – MINLP	BARON	BARON
Continuous variables	147	145
Integer variables	42	42
Computational time, s	199 459	51 986
Tolerance	0.01	0.001

4.5.3 Discussion

The use of a sequential algorithm allowed the distribution of complexity over two separate models. In the first model, the integer constraints were relaxed and the model was allowed to determine the optimal contaminant removal required. In the MINLP, the complicating variable RR_x was fixed and the integer constraints were reintroduced.

Within a reasonable margin of error, the sequential approach is able to produce near globally optimal solutions at less than half the computational expense required by the global optimisation solver. While some discrepancies in ED design and plant topology exist, the major cost functions and the overall objective functions differ by less than 4%. Based on this investigation, it is possible to use sequential algorithms to solve WRNS problems to perform preliminary design or budgeting estimates. However, there is no guarantee that for different case studies, the sequential algorithms will yield similar results. Therefore, for the detailed design, global optimisation methods are preferable.

4.6 References

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5

LIMITATIONS & RECOMMENDATIONS

5.1 Introduction

The purpose of this chapter is to highlight some of the limitations of the models and recommend ways in which to build on this work in future. Firstly, a discussion of assumptions made in the detailed ED model development is given. Computational challenges are addressed by considering both model formulation and solution strategies. A brief explanation of characteristics of common improper solutions and their associated diagnostic tools is presented. This is followed by a discussion of the solution strategies and computational platforms explored in this work. In conclusion, proposals for future research considerations are given.

5.2 Electrodialysis Model Assumptions

In this section a discussion is presented on the correlations and assumptions adopted in the electrodialysis design model.

5.2.1 Concentrate Concentration Profile

For the exact model development presented in Section 3.3.4, Formulation 1, it was necessary to determine the correlation between concentrate concentration at any point, C^c, and the concentration flux, C^y. This was done using the simplified model, Formulation 2. The correlation for the Kraft case study presented in Section 4.2.1 is given in Figure 5.2. A linear regression was applied to the model and the resultant equation embedded into the design model was given be Equation (5.1).

$$C^c = 6.15C^y + 1.09 \tag{5.1}$$

This regression corresponds to Equation (3.27), where $\tau = 6.15$ and $\omega = 1.09$.

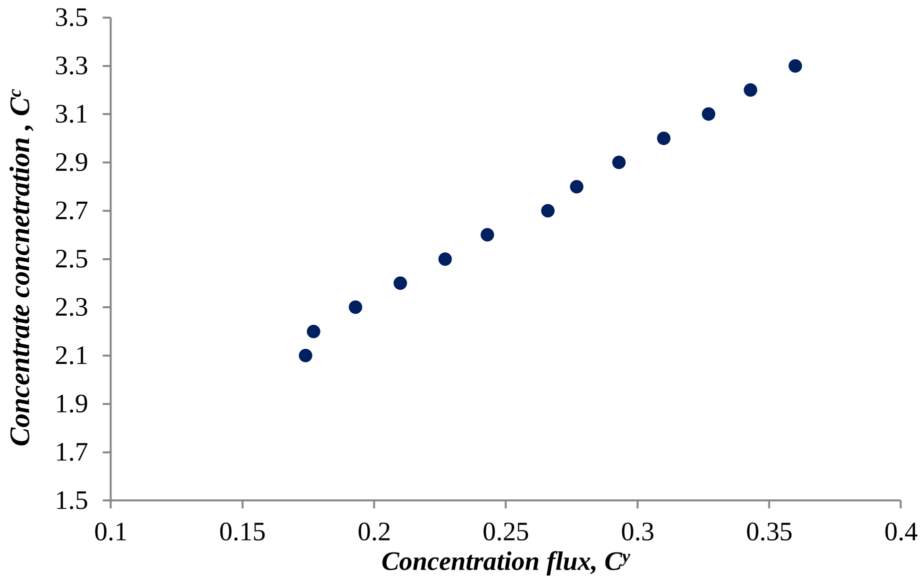

Figure 5.1: Correlation between concentrate concentration and concentration flux

This correlation is case specific and depends on the parameter values employed. It may therefore be necessary, when applying the exact model, to conduct a similar investigation based on the case study under consideration.

5.2.2 Parameter Values

Some of the electrodialysis parameters employed in the case studies are contaminant specific and must be experimentally determined. However, due to the unavailability of these parameter values in the absence of experimentation, parameters from the works of Lee et al. (2002) and Tsiakis & Papageorgiou (2005) based on sodium chloride were assumed. This was justified by the fact that in the case studies considered, effluent contained NaCl and similar salts. These parameters include the limiting current density constants, σ and φ, and combined membrane resistance, $\rho^a+\rho^c$. Lee et al. (2002) presented a range of membrane resistance values for the CEMs and AEMs calculated based on either NaCl or KCl solutions. An average value of $7\Omega cm^2$ was selected, and this value was used in the case studies. The authors also presented the results of an experiment conducted to calculate the limiting current density constants based on a range of concentrations of NaCl solutions. In order to observe the effect of these parameter values on the model, a sensitivity analysis was performed using the single contaminant model of Tsiakis and Papageorgiou (2005).

Figure 5.2 shows the sensitivity analysis conducted for the current density constant, σ. The analysis shows the effect of up to 10% deviation from the base value, 25 000, on key variables and total ED cost. Financially, incorrect estimation of this constant has no significant impact. However, from design perspective, a 10% inaccuracy in parameter valuation can lead to up to 60% deviation in pressure drop from the optimal value. A similar relationship was observed for the other limiting current density constant, φ. For the combined membrane resistances, no significant impact was observed on key variables and cost following 10 % variation in the assumed value. Based on this analysis, it is recommended that if the detailed ED model is adopted for a detailed design beyond order of magnitude estimates for complex, multicontaminant feeds, appropriate constants, σ and φ, must be obtained.

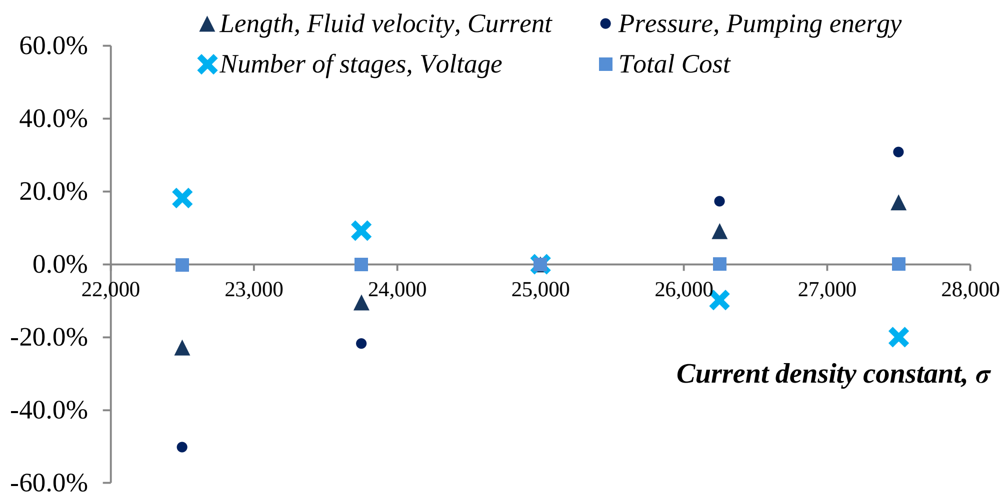

Figure 5.2: Sensitivity analysis indicating the effect of varying the current density constant, σ, on some variables in the electrodialysis model

5.2.3 *Electrodialysis Orientation*

The development of the ED design model was based on certain assumption of the electrodialysis stack orientation. These assumptions, listed in Subsection 3.3.2, include the following:

(i) Equal dilate and concentrate flowrates,
(ii) Co-current operation, and
(iii) Geometrically similar diluate and concentrate compartments.

As highlighted by Brauns et al. (2009), the above assumptions limit the applicability of the model in industrial cases. It is therefore recommended the model be expanded to allow flexibility in unit orientation.

5.3 Computational Challenges

A trend observed in the WNS case studies presented in Sections 4.3, 4.4 and 4.5 is that as model complexity increased, computational time increased. Increasing the model size, i.e. more sources, sinks and contaminants would result in increased nonconvexity. Consequently, this would further increase the computational time required to solve the model. It is worth noting that for grassroots and retrofit design problems that are conducted once-off, a long computational time may not be detrimental, as with regularly run models, such as scheduling problems. However, this drawback may still limit the applicability of the model to larger case studies. Computational challenges can be addressed by analysing and modifying the model itself or adapting the solution strategy, as will be shown below.

The MINLP models took significantly more time than the RMINLP models to solve, due to the presence of binary variables. Furthermore, the introduction of a variable removal ratio had a significant impact on the computational time. When removal ratio is variable, the Equation (5.2) contains a bilinear term on both the RHS and LHS. The introduction of this complicating variable increased the nonconvexity of the model significantly.

$$RR_x \sum_j C_{j,x} F_j^r = C_x^{r,con} \sum_i F_i^{r,con} \qquad \forall\ x \in X \qquad (5.2)$$

Critical variables can also be identified by observing the marginal values associated with the variables. The marginal value or Lagrange multiplier of a variable or constraint represents the rate at which the objective value changes with respect to that variable or constraint. It indicates the sensitivity of the objective to a particular variable or constraint. Variables found, at some point, to possess nonzero marginal values include current, current density, power, pressure drop, concentrate recycle, removal ratio and ED total cost. Some of the constraints governing stream interconnections also exhibited large marginal values.

5.3.1 Model Formulation

The structure of a model can be responsible for hindering solution progress. Common computational challenges will be discussed below, followed by challenges experienced in the case studies presented in this dissertation.

Common Unacceptable Solution Conditions

McCarl and Spreen (2011) highlighted main causes of obtaining improper solutions in mathematical models, as well as the techniques that can be used to diagnose these conditions. Four common undesirable model outcomes are:

i) *Solver failure.* Solvers often fail, citing numerical difficulties, ill conditioning, or a lack of progress despite using a large amount of resources (memory and time). Solver failure may also be caused by degeneracy-induced cycling. Degeneracy means that basic variables are equal to zero, and variables may become reductant. Cycling, in this respect, implies that the model becomes "stuck" and iterates excessively at a single point (McCarl, 1977).

ii) *Unbounded solution.* The solver fails to report a solution, stating that the problem is unbounded.

iii) *Infeasible solution.* The solver fails to report a solution, stating that the model is infeasible

iv) *Unsatisfactory optimal solution*. An optimal solution is reported, but upon observation of the variables, their values may be impractical. This may be due to omitted constraints or variables, algebraic errors or errors in coefficient estimation.

Seven techniques were then proposed to debug a model and identify the cause of undesirable outcomes.

i) *Structural checking*. The first step in model debugging involves analytical and numerical analysis of the model. Analytical checking involves observation of parameter values. Incorrect parameter estimation may cause a model to be infeasible, force a variable set to be zero, introduce redundant constraints, and result in unattractive variable outcomes. Numerical analysis can be performed by observing the relationships between variables and relevant equations as well as testing the homogeneity of units. Structural checks also include model verification, the process of determining that a model implementation accurately represents the conceptual description of the model.

ii) *A priori degeneracy resolution scheme*. Degeneracy related problems can be resolved by adding small numbers to the right hand side of equations to avoid redundancy. The magnitude of these artificial variables is informed by knowledge of the marginal values.

iii) *Scaling*. Scaling is necessary when there is a large disparity in the magnitudes of variable coefficients. As a rule of thumb, when magnitudes differ by a factor of 10^3, units of the variables and constraints must be changed. This results in the improvement of numerical accuracy and often reduces solution time. Scaling can be performed on the constraints, variables, or the objective function.

iv) *Artificial variables*. Large artificial variables can be added to a model formulation to overcome infeasibility. These variables allow the model to have a feasible solution regardless of whether the real constraints are satisfied. It is then possible to identify the constraints causing infeasibility.

v) *Upper bounds*. This involves the imposition of large upper bounds to variables presenting undesirable outcomes. The variables causing unboundedness can then be identified as they will take on large values.

vi) *Budgeting.* In this context, budgeting refers to the use of marginal values and variable outcomes to identify misspecifications in the model formulation. This requires insight into the case study under consideration, in order to identify impractically large marginal values.

vii) *Row summing.* When a variable has an unrealistically large solution value, the constraints containing said variable can be summed to identify incorrect coefficients.

Based on the identified challenges, McCarl and Spreen (2011) presented a table suggesting of the order in which to apply each of the seven techniques when diagnosing improper model solutions. This is presented in Table 5.1, where the technique to be tried first is numbered 1 and so on. While some of these techniques can be applied automatically by solvers, many require manual execution and insight into the physical conditions described by the constraints. Model validation is beneficial in this regard; to observe how accurately the model outcomes represent the real life case. Following structural and other checks, it may be necessary to reformulate the model.

Table 5.1: Priorities of techniques to use to diagnose improper model solution outcomes (McCarl and Spreen, 2011)

	Structural check	Degeneracy resolution	Scaling	Artificial variables	Upper bounds	Budgeting	Row summing
Solver failure	1	3	2	5	4		
Unbounded solution	1		3		2		
Infeasible solution	1		3	2		4	5
Unsatisfactory optimal solution	1					3	2

Computational Challenges Faced in this Work

Upon observation of the solution log produced by GAMS ® when using BARON, it was possible to analyse the quality of the solution as the iteration progressed. In most cases, the lower bound reached its optimal value early in the process, and the upper bound experienced cycling i.e. there was marginal relative improvement between successive iterations. This solver failure implies that the main challenge was in the solution of the exact problem. Also, this implied that an appropriate convex relaxation technique was applied – since the lower bound in BARON corresponds to the convex relaxation of the exact problem.

Following structural analysis of early versions of model, it was reformulated. For example, hard bounds were introduced to bilinear constraints in the WNS problem to reduce the problem search space (Equations 3.121-3.124). Numerical analysis by testing the homogeneity of units was also performed. Other methods employed include objective function scaling, constraint scaling and the variation of upper bounds to locate infeasibilities. Artificial variables were also added to some constraints to avoid redundancy. Following these diagnostic techniques, parameter values and variable bounds were adjusted accordingly and some constraints were reformulated.

If cycling were observed in the iterations of the lower bound, it may be necessary to introduce alternative convexification methods. Alternatively, one could generate a separate solution to the convexified problem and use it to provide a lower bound or initial value for the objective function of the exact MINLP.

5.3.2 Solution Strategies

The solution procedure and computational platform employed contribute significantly to the resources required to solve a particular model.

Sequential Approaches

As described in Chapter 4, a combination of direct global optimisation and sequential algorithms were used in this work. In addition to these, Figure 5.3 presents two sequential strategies that were attempted.

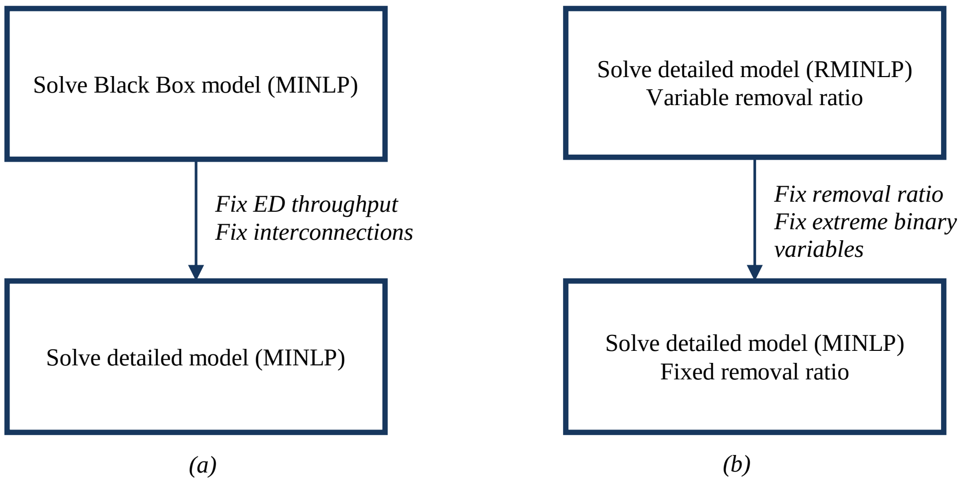

Figure 5.3: Possible sequential algorithms for the solution of integrated WNS problems

According to the algorithm given in Figure 5.3(a), a black box model was first solved as an MINLP. The values of the ED feed flowrate and the binary variables were fixed and input to the detailed model. While this reduced the computational time, the reliance of this algorithm on simplified cost functions in the black box model to determine plant topology decreased confidence in the optimality of the solution.

Alternatively Figure 5.3 (b) proposed that the relaxed detailed model be solved with variable removal ratios. The obtained values for *RRx* were input to the MINLP. The RMINLP was also be used to fix the binary variable that took on the values of 0 and 1, to reduce the number of integer variables in the exact model.

The second algorithm was further improved by employing the *adaptive numerical optimization procedure* described by Arora and Tseng (1988). This is an iterative method that involves the initial solution of an RMINLP. Binary variables with a value relatively close to their integer value are fixed at 0 or 1 respectively, then the RMINLP is executed again. This process is to be continued until all variables discrete variables have been assigned accordingly. In the current research, this method proved unsuccessful; later iterations yielded unfeasible results. The disadvantage of this approach is the possibility of fixing interconnections in early iterations that yield unfeasible or suboptimal results in the final solution, as was the case in this work. Furthermore, the cumulative computational time required was more than the time required to solve the model directly.

The advantage of sequential approaches is that they distribute the complexity over two less complex models with the potential, but no guarantee, of decreasing the overall computational time. However, they cannot guarantee global optimality. For larger and more complex problems, it may prove beneficial to explore sequential and iterative techniques that may be able to provide near global optimal solutions.

Pre-processing

Pre-processing involves steps taken before solving a model that result in the improvement of the quality of the final solution or reduced computational intensity. Some steps that may be taken include:

- Range reduction by introducing tight bounds to key variables
- Exact linearization of nonlinear terms, if possible
- Initialisation of variables by the use of graphical methods, solving convex relaxations manually and applying physical insights or other heuristics
- Reformulation of model constraints their simplest form to avoid redundancy.

Computation Platform

The models in his work were run on a personal computer with the following specifications:

Processor: Intel® Core ™ i7-3770 CPU@ 3.40GHz (4 cores)

RAM: 8 GB

System type: 64 Bit Operating System Windows 7 Professional

Optimisation platform: GAMS® v24.2.2

A multi-core processor is able to perform several tasks simultaneously. Considering that most global optimisation solvers decompose models into sub-models, the use of multiple cores provides additional processing capacity for these models. This parallel processing would potentially reduce the solution time required. One example of the use of a computational grid of parallel computers in solving WNS problems was given by Khor et al. (2012b). In this work, a computational grid containing 70 computing nodes, mostly running on 12-core 3.47 GHz Intel® Xeon™ X5690 processors with 4–128 GB of RAM was used. However, this model, with over 1036 bilinear terms, still took over 11 days to solve to completion. The default operation of many GAMS solvers is that they only use a single core of the processor, despite the hardware capacity. However, the most recent version of BARON, version 15.6.5 allows parallelisation of the model by specifying the number of "threads" the solver employs (Sahinidis, 2015).

A web-based optimisation platform was also explored. The NEOS server, hosted by Wisconsin Institutes for Discovery at the University of Wisconsin in Madison provides remote access to high performance parallel computing services (Czyzyk et al., 1998; Gropp and More, 1997). However, this server limits the job processing time to 8 hours. Due to the fact that models presented in this dissertation required more time than this limit, the NEOS server was not employed for the final case studies.

5.4 Recommendations for Future Work

The following recommendations are proposed in expanding the scope of the work presented in this dissertation:

i) It is recommended that the formulation be further developed to include multiple, variant regenerators, with different feed criteria. Building on the black box-based work of Khor et al. (2012), a subnetwork of regenerators can be developed. The overall framework would be able to select the appropriate treatment units based on the contaminant requirements of the sinks, the cost of regeneration, and the energy requirement. A comprehensive detailed membrane network for wastewater treatment, without a background process, has been presented by Koleva et al. (2015).

ii) In order to overcome the trade-off between computational time and accuracy, the exploration of grey box models of treatment units in WNS is suggested. This concept, presented by Yang et al. (2014) can be modified to include enough constraints in the formulation to adequately capture simultaneous design and energy minimisation. Grey box models may be used in conjunction with the proposed sequential and iterative models, instead of the black box models.

iii) The ED model in this work considered only a binary mixture of simple salts. The model formulation may be expanded to include more complex mixtures, as well as multiple ED stack orientations.

iv) Having identified the importance of removal ratio in obtaining the optimum solution, it is recommended that the formulation be expanded to consider WNS uncertainty, owing to variation of removal ratio on a plant. A black box example is presented in the work of Khor et al. (2014).

v) The objective cost function used in this formulation considers the capital and operating costs of the water network. In order to truly evaluate the long term profitability of retrofitting a regeneration unit to a plant, the economic framework could be expanded to calculate the net present value, rate of return on investment and other profitability indicators.

vi) The framework could be modified to allow the inclusion of pre-treatment of freshwater and end-of-use wastewater treatment. This corresponds to the upgrade of the model from a regeneration water network to a complete water system.

vii) Disposal of effluent in rivers may be associated with some taxation or penalty. The formulation can be modified to include these factors. Some companies may be able to pay these penalties to avoid redesign. Given the social pressure companies face to operate sustainably, this may negatively impact their reputation. If a monetary value is assigned to reputation, this can also be factored into the overall objective function.

To improve computational efficiency, these additional recommendations are presented:

viii) It is recommended that parallelisation of the model be explored in order to exploit available super computing platforms

ix) Exploration of integrated solution strategies and pre-processing methods to reduce computational resources required.

x) To reduce the computational requirement of the model, the exploration of other global optimisation strategies for WNS is recommended. For example, generalized disjunctive programming (GDP) is a logic based method for representing constraints with discrete variables in optimisation problems. GDP has been applied successfully to WNS problems in the works of Karuppiah & Grossmann (2006) and Yeomans & Grossmann (1999).

xi) Alternative methods to ease computational difficulty include the use of metaheuristic algorithms, that provide near-optimal solutions at low computational cost. This includes the use of genetic algorithms (GA), a global search method that mimics natural selection to obtain an optimum solution from a population of candidate solutions. Tsai and Chang (2001) used genetic algorithms to optimize a water use and treatment network in a way that minimized the solution search space. Luus-Jaakola Adaptive

Random Search (ARS) algorithms involve iteratively reducing a solution search space around the current best solution (Poplewski and Jezowski, 2010). The iteration points are generated using a uniform probability distribution. An example of ARS in NLP water allocation problems was presented by Poplewski and Jezowski (2005).

xii) In order to cater for long term uncertainty associated with price fluctuations of commodity prices and the variation of contaminant loads in water networks, it is recommended that more robust optimization methods are considered. For example, Koppol and Bagajewicz (2003) used a probability distribution based on various scenarios of an uncertain term, it is possible to determine which water allocation design presents minimal financial risk.

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6

CONCLUSIONS

The objectives of this study were as follows:

(i) To develop a detailed, standalone optimisation model of a multicontaminant electrodialysis unit to minimise operation and capital costs. In so doing, it is desired to obtain the optimum operating and design conditions of the electrodialysis unit including current, voltage length, area and the number of cell pairs.

(ii) To develop a complete water network superstructure which is the basis for a mathematical optimisation approach for water minimisation.

(iii) To integrate the electrodialysis standalone model with the water network superstructure in order to develop an approach for simultaneous water and energy minimisation in a water network. The overall objective function, expressed as a cost function, minimises the amount of freshwater consumed, wastewater produced, the energy consumed in the regeneration unit and the piping costs (both capital and operational), associated with retrofitting the new plant design.

A novel electrodialysis design model for multiple contaminants was developed from first principles. Two formulations were presented based on different assumptions of solution conductivity. Formulation 1 is an exact derivation which was found to be mathematically and computationally intensive. This formulation is best suited for a standalone ED design where the feed contains simple salts. Formulation 2 makes a simplifying assumption the concentration difference over an ED unit is sufficiently small that conductivity can be assumed constant. This formulation is more flexible and is easily adaptable to cases with complex salts. The computational requirement is less than Formulation 1 and it is therefore better suited when being combined with a background process. A comparison was drawn between the two formulations based on a chloride removal case study in a Kraft paper plant. It was found that the models yielded similar results with deviations of up to 3% for key variables.

The ED model, Formulation 2, was embedded into a water network problem. Mathematical optimisation techniques were used to develop a superstructure comprised of multiple sources, sinks and a treatment unit. In order to emphasise the inefficiency of the commonly used black box approach, the developed WNS model was applied to a pulp and paper case study. Four scenarios were presented as follows:

- *Base case:* No process integration
- *Scenario 1:* Water minimisation only
- *Scenario 2*: Water and energy minimisation with a fixed removal ratio
- *Scenario 3:* Water and energy minimisation with a variable removal ratio, solved using direct global optimisation
- *Scenario 4*: Water and energy minimisation with a variable removal ratio, solved using a sequential solution procedure.

Based on the above scenarios, the following conclusions were drawn:

- Designing the regeneration unit within the water network minimises both the water and energy consumption simultaneously.

- Representing a regenerator using only removal ratio expression neglects key aspects of regeneration units, and this results in the underestimation of the amount of energy required in the water network. Discrepancies of up to 80% were observed. For accurate representation, a detailed design model is required.
- Using global optimisation with less than 0.1 % tolerance, the developed model results in 38% savings in freshwater consumption, 68% reduction in wastewater production and 55% overall cost reduction when compared with the original pulp and paper plant presented in the case study.
- In addition to water reduction, the integrated approach resulted in an 80% reduction in the regeneration and energy cost.
- By allowing the removal ratios to be variable, the overall efficiency is improved as the regeneration unit is designed specifically for the demands of the sinks, as opposed to a generic design.
- Sequential solution procedures may reduce computational expense in WRNS problems and can be used for preliminary designs. However, for detailed grassroots and retrofit design problems, global optimisation of the integrated model with variable removal ratio is most appropriate.

The integrated water regeneration network synthesis model that was presented is able to produce significant reductions in water, energy, effluent production and cost. However, based on the fact that the global optimisation of a relatively small case study presented took over 55 hours to solve, it is necessary to improve the solution procedure in order for the model to be applicable to large problems. The potential for improvement was explored by the use of a sequential procedure, based on removal ratio values. Suggestions presented for further reduction of computational strain include

- Pre-processing for variable range reduction and good initialisation,
- Exploring other global optimisation solvers and strategies, such as GDP,
- Employing sequential and iterative solution procedures, and
- Parallel processing and the use of a strong computing platform.

In addition to improving the solution strategy, avenues for improvement and further development of the model scope were suggested. These recommendations include but are not limited to the following:

- To expand the electrodialysis model to cater for solutions with more than two contaminants
- To expand the scope of the problem by the inclusion of a complete membrane network
- To perform complete water system synthesis by including pre-treatment and end of use effluent treatment.