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OPTIMUM WATER NETWORK DESIGN FOR MULTIPURPOSE BATCH PLANTS WITH A DETAILED ELECTRODIALYSIS REGENERATION MODEL

Nsunda Christie Bazolana

(572003)

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

Supervised by: Professor Thokozani Majozi

June 2018

Declaration

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

……

(Signature of Candidate)

……day of……..year……..

Abstract

Stringent environmental regulations and economic expansion in the recent decades has justified the need for sustainable water usage in the process industry. The usage of water in multipurpose batch plants is essential in cleaning operations to ensure the integrity of various tasks processed in multipurpose units by avoiding contamination between consecutive batches. This usually requires a considerable amount of water while generating highly toxic effluents. The minimization of water in batch plants is achieved through direct, indirect and regeneration reuse. These techniques are mainly dependent on the schedule of the plant and a flexible schedule usually guarantees an increase in water saving opportunities. While direct and indirect reuse requires capital investments, regeneration reuse involves additional operational costs through the consumption of intensive amount of energy. It is therefore vital to capture the trade-off between water and energy usage and explore their respective cost implications.

This work presents a Mixed Integer Nonlinear Programming (MINLP) formulation that simultaneously optimizes the production schedule and utility consumption in multipurpose batch plants. The amount of wastewater generated in batch operations is minimized through the exploration of direct, indirect, and regeneration reuse opportunities within the plant. Water regeneration is achieved through partial purification of highly contaminated wastewater using electrodialysis. A design model for electrodialysis is included in the formulation in order to allow for simultaneous optimization of water and energy use in the regenerator. The formulation is first applied to two examples from literature for validation. Freshwater savings of 37.4 % and 41.1% are achieved in each literature example while maintaining the revenue at its maximum value. The efficiency of the designed regenerators with respect to their energy consumption is evaluated by comparing the proposed technique with a case where the minimization of energy is not considered. A reduction in energy consumption by 31.6 % and 9.8% for both examples is respectively observed. A

study is then undertaken at Amul plant, one of the biggest dairy in the world, in order to assess the practicality of the formulation. The formulation is applied to the raw milk receiving department (RMRD) where the highest amount of freshwater is consumed. Freshwater and energy savings of 38 % and 95.2% are achieved under the consideration of a single quality of water streams. An economic analysis of the integrated water network is performed and 20 % reduction in the total operating cost of the RMRD is achieved through the implementation of the proposed water minimization technique.

Dedication

To my parents,

Jean-Pierre Bazolana Mandangi and Veronique Mputu Modiri

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List of Abbreviations

RMRD	Raw Milk Receiving Department
LCA	Life Cycle Analysis
ED	Electrodialysis
MINLP	Mixed Integer NonLinear Programming
LP	Linear Programming
NLP	Nonlinear Programming
IP	Integer programming
MILP	Mixed Integer Linear Programming
PIP	Pure Integer Programming
MIP	Mixed Integer Programming
BB	Branch and Bound
GDB	Generalized Benders Decomposition
OA	Outer Approximation
ECP	Extended Cutting Plane
SGO	Signomial Global Optimization
PLF	Piecewise Linear Function
GAMS	General Algebraic Modelling System
AMPL	A Mathematical Programming Language
BARON	Branch And Reduce Optimization Navigator
DICOPT	Discrete and Continous OPTimizer
ER	Equality Relaxation
AOA	AIMMS Outer Aproximation
SBB	Simple Branch and Bound
ANTIGONE	Algorithm for coNTinuous /Integer Global Optimization of Nonlinear Equations

NIS	No Intermediate Storage
IS	Intermediate Storage
FIS	Finite Intermediate Storage
UIS	Unlimited Intermediate Storage
CIS	Common Intermediate Storage
PIS	Process Intermediate Storage
MIS	Mixed Intermediate Storage
ZW	Zero Wait
FW	Finite Wait
UW	Unlimited Wait
STN	State Task Network
SSN	State Sequence Network
RTN	Resource Task Network
CPU	Central Processing Unit
CIS	Critical Intermediate State
WCA	Water Cascade Analysis
CIA	Concentration Interval Analysis
WAN	Water Allocation Network
DC	Direct Current
CEM	Cation-Exchange Membranes
AEM	Anion-Exchange Membranes
RO	Reverse Osmosis
NF	Nanofiltration
CEPCI	Chemical Engineering Plant Cost Index
CIP	Cleaning In Place
TSS	Total Suspended Solids
TDS	Total Dissolved Solids

COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
UF	Ultrafiltration
MSA	Mass Separating Agent

1

INTRODUCTION

1.1 Background

The chemical industry is one of the largest contributors to the economy of the world. It converts raw materials into a wide variety of products that can be further processed by other industries or readily used by consumers (Bonvin, et al., 2006). Chemical processes are broadly subdivided into batch and continuous processes. Continuous processes gained popularity in the early ages due to the predominance of constant and high demands of products in the global market. However, in the recent past, the demand for high value-added products in low volume by major markets has triggered the need for flexible production schemes such as batch processes. There has since been a growing interest towards the development and optimization of batch chemical processes (Majozi, 2010).

The optimization of batch chemical processes with respect to their water consumption greatly contributes to environmental conservation. Water crisis is being experienced worldwide where industrial development and population growth are increasing the freshwater demand and effluent generation (UNEP, 2010). This leads to hazardous impacts on the environment such as the release of unwanted pollutants and scarcity of freshwater sources which can possibly cause serious damage to human health and

result in a lack of accessibility to clean water and sanitation (UNEP, 2010). In South Africa, for instance, there is a growing pressure to meet the water demand of an increasing population and various industries. The availability of clean water is being stressed by the scarcity of rainfall, industrial pollution and the lack of sanitation in rural regions (Admin, 2012; Project, n.d.). Therefore, the drive towards cleaner production for the prevention of environmental pollution, and sustainable usage of water is pertinent. An efficient use of water also results in a highly profitable industrial process whereby operating and environmental costs are minimized (Chatuverdi & Bandyopadhyay, 2014b).

The minimization of wastewater generation in batch processes is an effective strategy for the prevention of environmental pollution. Washing of multipurpose units at certain time intervals is essential in batch production to conserve the integrity of a batch and maintain a required hygiene standard. These operations usually result in the generation of highly toxic wastewater effluents (Majozi, 2010). Wastewater minimization in batch plants is mainly achieved by implementing process integration techniques such as direct, indirect and regeneration reuse while considering a predefined or unknown schedule of batch operations. Direct reuse of water entails direct water transfer between a source and a sink provided that the finishing time of the unit acting as a water source and starting time of operation acting as a water sink coincide. In this context, a source refers to any batch operation that can potentially generate wastewater whilst an operation requiring water is referred to as a sink. Indirect reuse then allows effluents from a unit to be stored for a period of time and later reused in another unit. Regeneration reuse requires partial treatment of effluents to reduce their contaminant level and further increase reuse opportunities (Adekola & Majozi, 2011).

Process integration techniques for the minimization of water use involve the use of energy due to the intricate connection that exists between both resources. A life cycle analysis (LCA) performed by Gleick (1994) on water and energy showed that

freshwater is strongly required in the energy sector. It is used for the mining of energy resources, as a feedstock to modify fuel properties, for cooling in power plants and for the operation and maintenance of energy-generation facilities. On the other hand, a substantial amount of energy in the form of heat or electrical energy is inputted into water supply and purification facilities for the desalination, pumping, and transfer of water. Furthermore, the process of reducing wastewater generation and freshwater use can potentially increase the consumption of energy through wastewater treatment facilities. The increasing demand for water not only restricts the amount of water available for the production of energy but also increase the overall energy consumption. Therefore, due to the high costs of energy globally, both resources need to be integrated when establishing policies for environmental protection (Gleick, 1994).

1.2 Motivation for the study

Substantial work has been directed towards the development of wastewater minimization techniques for batch water networks to ensure a sustainable use of freshwater resources by batch processes. However, many of the existing techniques do not consider the schedule for the background process. In other words, the process schedule is usually assumed to be fixed. A fixed schedule technique entails that the starting and finishing times of all tasks involved in a batch process are known prior to water network optimization. Their main drawback is the fact that process integration opportunities are to be found amongst operations that satisfy the necessary timing conditions for integration before optimization. These techniques are therefore not flexible and often result in less amount of freshwater reduction. Allowing the schedule of a batch process to be simultaneously optimized with the water network increases opportunities for freshwater reduction.

Regeneration reuse has also not been adequately considered in the published literature. In situations where regeneration reuse was considered, a “black-box” instead of a detailed regenerator model has been used. A “black-box” approach

entails modelling the performance of a regenerator using a fixed removal ratio of contaminant or fixed outlet concentration of purified water. An ideal performance of the regenerator is often assumed wherein no loss of water during regeneration occurs which entails that the waste stream from the regeneration unit has zero water content. The cost of regeneration is then estimated using a linear cost function which solely depends on the amount of water fed into the treatment unit. These techniques are therefore inefficient for the minimization of the energy consumption of the regenerator.

Figure 1.1(a) gives a schematic diagram of an integrated water system which includes regeneration reuse. Freshwater fed to the process and effluent generated from the process are the key variables to be minimized. A portion of wastewater generated within the process is transferred to the regeneration process where the contaminant level is reduced and returned to the process to minimize both freshwater and effluents. In many instances, the regeneration cost depends on the amount of energy inputted in the treatment unit for the purification of wastewater. The extent of energy usage in regeneration units, on the other hand, strongly depends on the total amount of water fed into these units and the required degree of purity of the regenerated water. As shown in Figure 1.1(b), the amount of energy used by the regenerator increases with decreasing freshwater intake and effluent generation and vice versa. Furthermore, the cost associated with energy consumption greatly contributes to the overall cost of an integrated water network. Therefore, the minimization of energy within water networks when exploring regeneration reuse is pertinent.

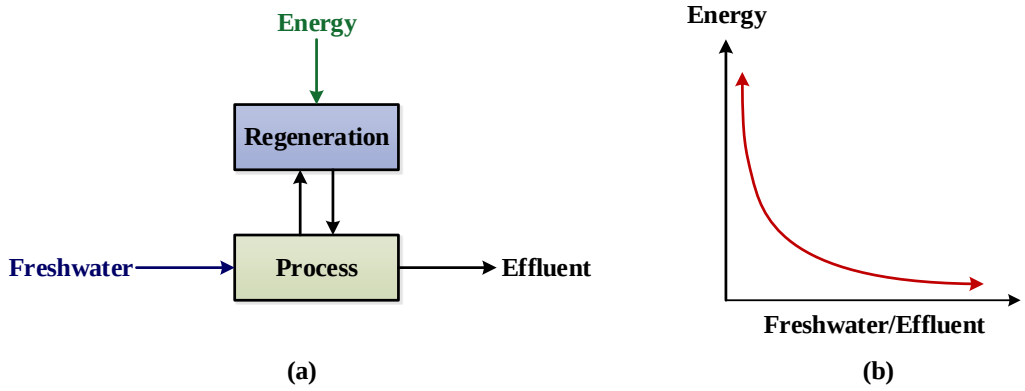


Figure 1.1 *Motivation for the study*

This work aimed at maximizing the performance of multipurpose batch plants by simultaneously optimizing the production schedule and the batch water network. Freshwater consumption is minimized by exploring direct, indirect and regeneration reuse within the plant. Regeneration reuse involves the partial purification of wastewater using an electrodialysis (ED) treatment unit. A cost-effective plant design is therefore guaranteed by ensuring that the production revenue is maximized and the trade-off between freshwater and energy consumption of the ED unit is captured for the minimization of the overall cost of the water network.

1.3 Research objectives

This research has achieved the following objectives.

- ❖ The development of a mathematical model for scheduling of multipurpose batch processes.
- ❖ The development of a model for a batch water network design and synthesis where direct, indirect and regeneration water reuse opportunities are explored and an electrodialysis (ED) design model is imbedded.
- ❖ The integration of the scheduling model with the water network design model in order to generate an overall formulation optimizing the schedule and water network simultaneously.

- ❖ The evaluation the overall model using literature examples and industrial case studies.

1.4 Problem statement

The problem addressed in this work can be stated as follows.

Given:

(i) The production recipe for each product, the available processing units, and their capacities,
(ii) The processing time and washing time in each unit,
(iii) The maximum storage capacity for each material,
(iv) The mass load and maximum concentrations of each contaminant,
(v) The available water storage tanks and their design capacity limits,
(vi) Membrane properties and design parameters of the electrodialysis (ED) regenerator, and
(vii) The time horizon of interest,

It is required to determine the optimum schedule of a multipurpose batch plant that yields maximum performance, i.e. a network design with minimum water and energy consumption, the optimum design of the electrodialysis regenerator and the optimum sizes of storage tanks. Optimum design of the regenerator, in this case, implies minimum energy use of the regenerator.

1.5 Dissertation layout

This dissertation comprises seven chapters. Chapter 2 gives a detailed literature review on the relevant aspects of this work. Chapter 3 presents the development of a mathematical formulation aiming to design and synthesize a cost-effective batch process. The concept behind the scheduling framework adopted is briefly explained followed by a detailed explanation of mathematical constraints pertaining to water

network integration, electrodialysis process design, and plant scheduling. Chapter 4 provides an illustration of the effectiveness of the proposed formulation by validating it using two literature examples. Chapter 5 presents an industrial case study to which the proposed wastewater minimization approach was applied to demonstrate its effectiveness and practicality in real-world scenarios. Chapter 6 then gives the pros and cons of the developed formulation as well as some recommendations for future work. Chapter 7 finally provides the dissertation with a conclusive summary highlighting the major components of the presented wastewater minimization technique.

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2

LITERATURE REVIEW

2.1 Introduction

The work of this dissertation contributes to water sustainability through the development of a mathematical programming model aiming to optimize the production schedule and water network of multipurpose batch plants. A literature analysis is conducted in this chapter to review the various techniques that have been established for the synthesis, design, and optimisation of batch chemical processes. The chapter starts by giving a background theory on batch processes, the different types of batch plants existing in the process industry and the various techniques used to represent key components considered during the optimisation of batch processes. The time dimension, an essential component of batch processes, is captured through the scheduling of batch operations. Hence, the subsequent section discusses the various techniques developed for the scheduling of batch processed. Next, a detailed review of the different methodologies developed for the minimisation of freshwater usage in batch processes is presented. The regeneration process of focus in this study, i.e. Electrodialysis, is then elaborated alongside with its applications, advantages, limitations and existing design models. The chapter ends with a section discussing the various solution approaches to wastewater minimisation problems.

2.2 Batch processes

2.2.1 Background and definition

Continuous and batch processes are the two major constituents of chemical processes. Continuous processes are mainly used in industries which aim to manufacture large quantities of products such as petroleum and metallurgical industries. This is a result of the fact that they are maintained at an economically desirable operating point and thus require substantial effort in the design phase. Batch processes, on the other hand, are more suited for the production of chemicals in low volumes. They allow for materials to be sequentially fed to, processed into and discharged from a processing unit as illustrated in Figure 2.1. Consequently, batch processes enable the adjustment of operating parameters such as temperature and processing time. Therefore, batch processes exhibit more flexibility than their continuous counterpart from the operational point of view (Bonvin, et al., 2006).

A batch process is defined as any process whereby discrete tasks occur according to a predefined sequence from raw material to final products. The predefined sequence of tasks is usually referred to as a recipe. The industrial attraction of batch processes resides in their ability to produce a wide variety of products within the same facility due to their intrinsic flexibility. This renders them suitable to accommodate fast changes and variable needs in the global market. Batch manufacturing is mainly used in pharmaceutical, food, polymers and specialty chemical industries since the demand for the manufactured products in these industries is highly seasonal and strongly influenced by changing markets (Seid & Majozi, 2014). Examples of specialty chemicals include plastics, paints, cosmetics, printing ink, dyes and lubricants (Bonvin, et al., 2006)

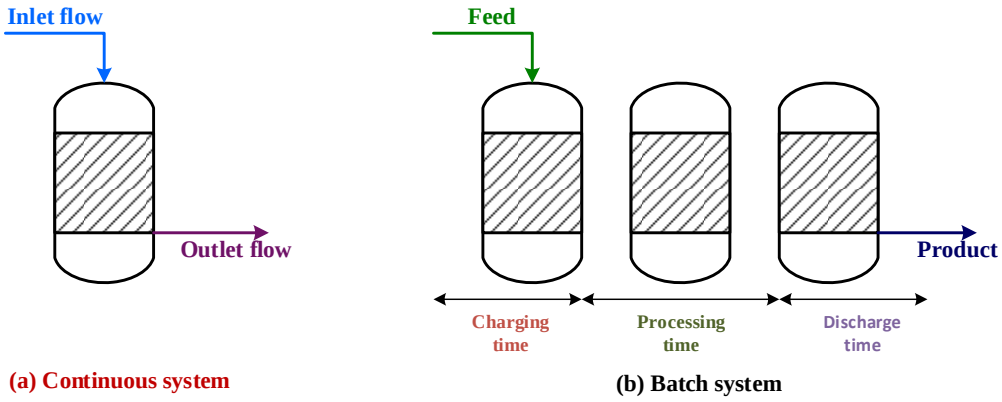


Figure 2.1 *Analogy between continuous and batch processes*

2.2.2 Classification of batch processes

Batch plants are broadly classified into multiproduct and multipurpose plants. In multiproduct batch plants, each batch of product manufactured follows the same recipe whereas multipurpose batch plants allow for the variation of production recipe of one product from one batch to the other. Therefore, multiproduct facilities are suitable for the production of products with a fixed and identical recipe while multipurpose facilities are more appropriate for production environments characterized by a variation in the recipe (Majozi, 2010). The above descriptions stipulate the evidence of the complex nature of multipurpose batch plants when compared multiproduct plants. This statement is also applicable to their resultant mathematical formulations. Therefore, formulations developed for multipurpose batch plants can be readily adjusted to suit multiproduct plants whereas the opposite is not valid. For the aforementioned reasons, it is commonly suggested that substantial efforts be directed towards the development of optimization techniques for multipurpose batch plants (Majozi, 2010).

Batch processes existing within a given plant are classified based on the topology of batch tasks involved in the production of one or many goods. Multiproduct batch plants are usually made of sequential processes (Mendez, et al., 2006). A sequential

process is a process whereby a given batch cannot be mixed with other batches or split to form multiple batches. Sequential processes can be set up in a single stage or have multiple stages of operation. A single stage batch process consists of a set of units arranged in parallel with each unit performing exactly one task or batch. A multistage process, on the other hand, is made of multiple stages of parallel units. Similar to single stage processes, a unit can only perform one task in multiproduct plants with multiple stages. Multipurpose processes can either have a sequential or network configuration. In some instances, both configurations coexist within the plant. A network process allows mixing and splitting of processed materials as opposed to sequential processes. Multipurpose batch processes, in general, allow units to be assigned to more than one operation (Harjunkoski, et al., 2014).

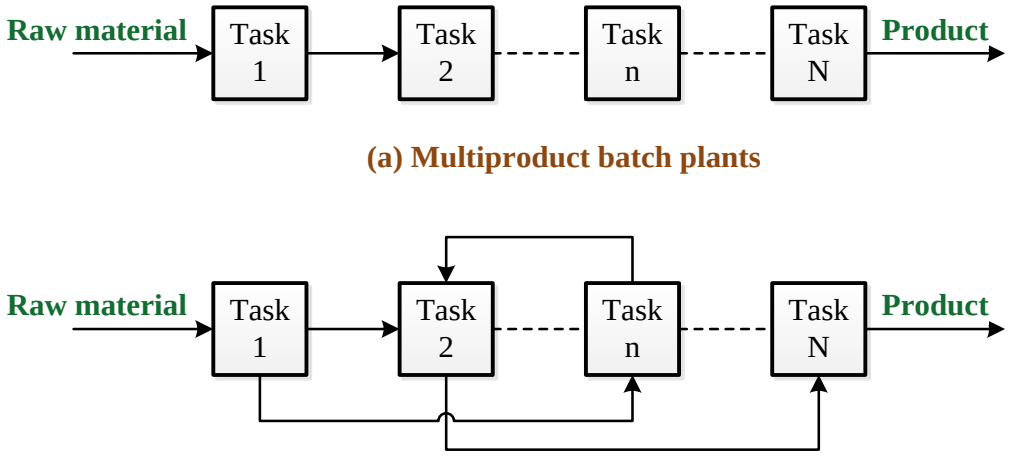


Figure 2.2 *Sequence of tasks in (a) multiproduct and (b) multipurpose batch plants (Majozi, 2010)*

2.2.3 Batch operational philosophies

Material transfer between various operations in batch manufacturing is an important aspect of the process schedule. The discrete occurrence of batch operations decreases

the degree of flexibility to transfer intermediate materials from one process to the other. This results from the fact that the completion of one task does not always coincide with the beginning of the subsequent task. This problem is generally overcome by the use of storage tanks; hence different operational philosophies were developed accordingly. The operational philosophies of batch processes are subdivided into two main categories, namely the No-Intermediate Storage (NIS) and the Intermediate Storage (IS). In the NIS, an intermediate material is allowed to wait in the producing unit until the next unit is available for the subsequent task, and it is usually adopted when there is limited space in the plant. The IS, on the other hand, allows materials to be stored in a dedicated tank.

The IS is further subdivided into Finite Intermediate Storage (FIS), Unlimited Intermediate Storage (UIS), Common Intermediate Storage (CIS), Process Intermediate Storage (PIS) and Mixed Intermediate Storage (MIS). The FIS allows for intermediate material to be stored in a dedicated storage tank of limited capacity before being fed to the next unit. The UIS on the other always ensures the availability of storage for an intermediate material. The CIS allows different intermediate materials to share the same storage tank within the plant. In this case, washing of storage tanks becomes essential to maintain the integrity of each task. The PIS explore the opportunity of storing intermediate materials into processing units that are not being utilized at specific points in time. The MIS, which is commonly encountered in batch plants, allows for any of the aforementioned IS to coexist within the batch facility.

The degree of stability of intermediate materials produced in batch processes determines the duration of material storage. Storage concepts taking this aspect into account include the Zero Wait (ZW), Finite Wait (FW) and Unlimited Wait (UW) philosophies. The ZW is adopted when an intermediate material produced is highly unstable. In this case, the finishing time of the task producing the intermediate needs to coincide with the starting time of the task consuming the intermediate product to

ensure direct consumption of the produced material. The FW allows the intermediate product to be stored for a limited period of time and is employed for partially stable materials. The UW is adopted for highly stable intermediates and allows them to be stored for a very long period of time (Majozi, 2010).

2.2.4 Recipe presentation

The recipe of batch network processes is complex and ambiguous due to the many interconnected tasks involved in a production cycle. Various techniques evolved in the past attempting to clearly represent the recipe of batch processes. This enabled the simplification of mathematical models for batch plant scheduling (Harjunkoski, et al., 2014). These techniques include the State Task Network (STN), the State Sequence Network (SSN), the Resource Task Network (RTN), the Schedule graph (S-graph), and the State Equipment Network (SEN).

The STN was proposed by Kondili et al. (1993) to improve the so-called "recipe network", a conventional way of representing batch recipe based on the concept used in the flowsheet representation of continuous processes. The STN provided a clearer representation of a batch recipe by using two types of nodes, the state node, and the task node. The state node represents the different materials processed within the plant, i.e. feed, intermediates and product materials. The task node, on the other hand, represents the operations conducted in one or various units for the transformation of one or more input materials into one or more output materials. Figure 2.3(a) gives the STN representation of a simple batch process made of 3 units processing one specific task each where one material is consumed by a task to produce another material. The STN uses circles and rectangles to graphically represent state and task nodes respectively.

The SSN representation of Majozi and Zhu (2001), is very similar to the STN. The difference resides in the fact that the SSN only uses state nodes to represent a

production recipe, as illustrated in Figure 2.3(b). States are used to denote materials processed and produced at each production stage as discussed in the description of the STN. The presence of a particular task is implicitly incorporated in the STN by the arc depicting a change from one state to another. This simplification resulted from the realization that the presence of a state in a particular operation implies that a task, which uses the state to produce another state, is being processed. Furthermore, the limiting capacity of a unit performing a task can be set by determining the maximum amount of states that a particular task can process. Mathematical models for batch process scheduling which adopt the SSN representation usually have a reduced number of binary variables which entails a reduction in the size of the model. This will be further discussed later in this chapter.

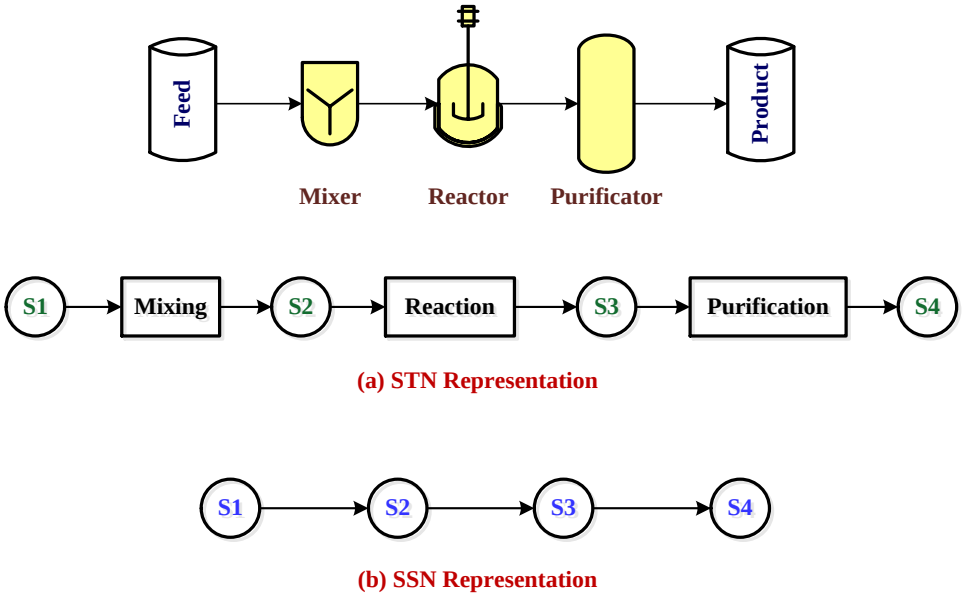


Figure 2.3 *STN and SSN representation of a simple batch process (Majozi, 2010)*

The RTN, proposed by Pantelides (1994), is an enhanced version of the STN. It provides a unified representation of all resources found in a batch process by consisting of a resource node and a task node. The resource node includes energy, transportation, processing units, cleaning, and storage equipment in addition to feeds,

intermediates and products. The task node is also generalised by including cleaning, transportation and other operations in addition to processing steps. Additionally, the RTN has the ability to clearly show resources that are shared by two or more task. Figure 2.4 gives the RTN representation of a batch process consisting of 3 tasks and 5 available units. It shows the flow of materials from one task to the other while giving information on the number of units available each task. For instance, task 1 converts raw material S1 into intermediate S2 and can be performed in both units J1 and J2.

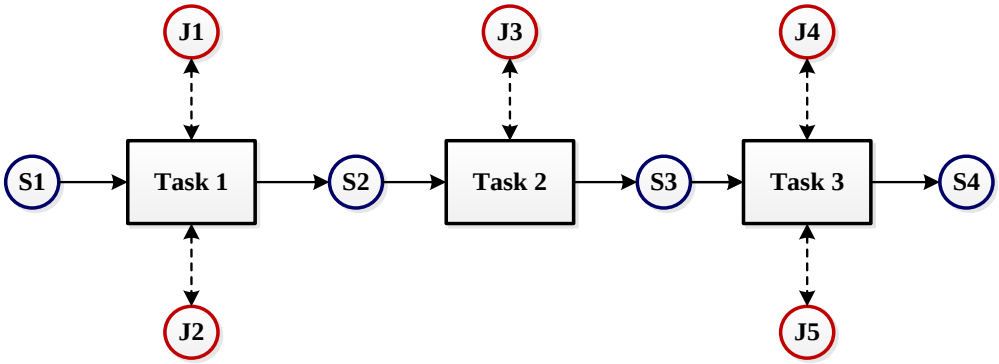


Figure 2.4 *RTN representation of a batch process (Shaik & Floudas, 2008)*

The S-graph, proposed by Sanmarti et al. (1998), represents a given production recipe with nodes and arcs as shown in Figure 2.5. Nodes are used to represent various production tasks while arcs show the precedence relationship between them. For each node, the node number and equipment unit processing the corresponding task are given in the graph. The processing time of each task is given by the number above each arrow connecting the task to its subsequent task. For instance, task 7, processed in unit E1, can only occur after the completion of task 1 in unit E1 and task 6 in unit E3. Additional nodes are included in the graph to represent the final products. These nodes are usually placed in the extreme right end of the graph and are connected to their producing tasks by an arc. The products of the production recipe represented by Figure 2.5 are given by nodes 4, 8 and 12. The S-graph, however, can only be applied to scheduling problems with NIS or UIS transfer policies.

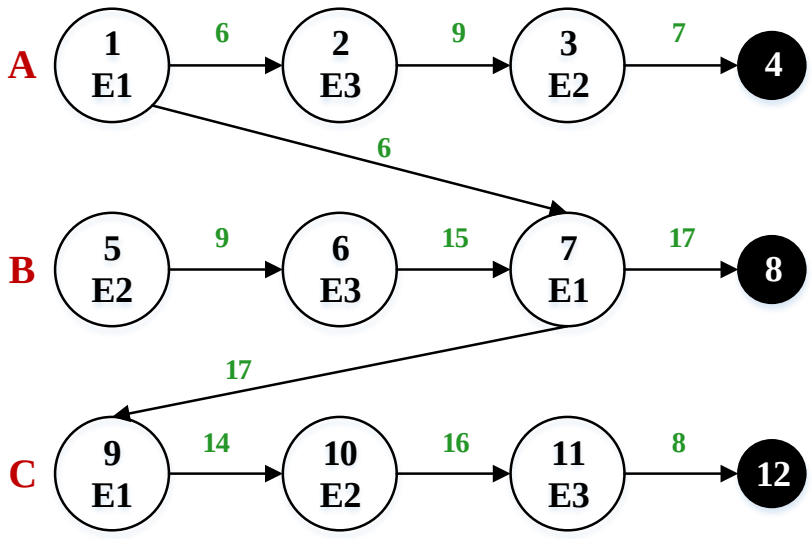


Figure 2.5 *S-graph of a batch production recipe (Sanmarti, et al., 1998)*

The SEN, similar to the previous representations, uses a bipartite graph comprising state and equipment nodes for the representation of a batch process. The state node includes all types of materials involved in a process while the equipment node is used for the representation of all processing units in the plant. The connectivity between the various nodes found in the SEN is subject to change over time. Due to the flexibility of batch processes, processing units usually undergo switching between operations, start-up and shut-downs at specific time periods. The SEN accommodates this aspect of batch processing by displaying the various operational states of a processing unit. The operational states indicate the possible operations a unit is suitable for, including the possibility of it being idle at a certain point in time. To provide a better understanding of the SEN representation of a batch process, a simple batch plant is depicted in Figure 2.6. The process comprises 3 processing units, namely a reactor, a filter and a distillation column. The distillation column is said to have different operational states. The column can either be used to process distillation 1 or distillation 2 at different time periods. The idle state of the distillation column is

not explicitly shown in the representation but is however considered as a possible operational state of the column (Nie, et al., 2012).

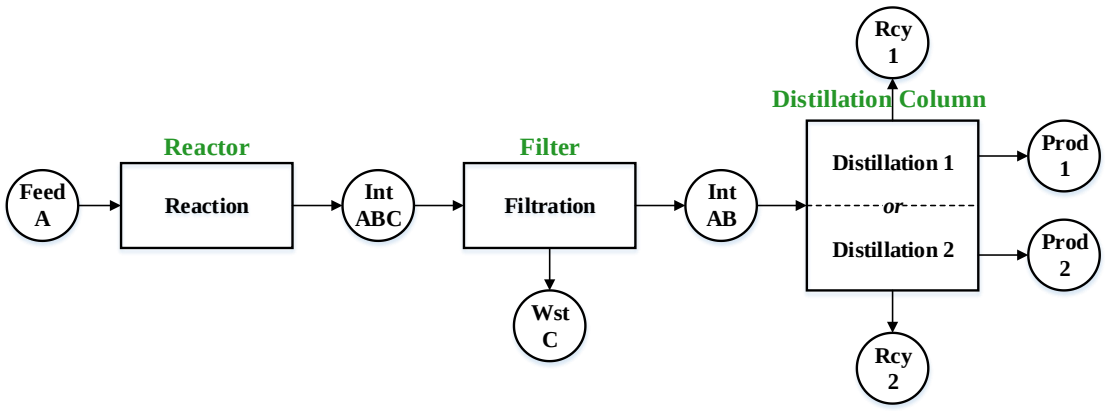


Figure 2.6 *SEN representation of a batch process (Nie, et al., 2012)*

2.2.5 Time representation

Time is the most important dimension considered in the development of mathematical models for batch process optimization. Different approaches have been established over the years as attempts to accurately represent the time dimension essential to batch processes. These approaches are broadly classified into discrete and continuous time formulations. Discrete time formulations rely on the even discretization of the time horizon of interest. This entails dividing the time horizon into a finite number of intervals of predefined duration, as illustrated in Figure 2.7 (Kondili, et al., 1993). In this time representation, tasks can only start and end at interval boundaries. This usually leads to a straightforward scheduling problem focussing on the allocations of tasks to predetermined time slots. However, the discrete time representation has the following shortcomings.

- The reduction in timing decisions, i.e. forcing events to only occur at time interval boundaries, could lead to suboptimal schedules due to lack of flexibility.
- An accurate representation of time can only be achieved with very small time intervals. This usually leads to large-scale models that are computationally intensive.
- Rounding up of task processing times is usually performed in discrete time modelling to reduce the size of the resultant problem formulation. This can lead to infeasible production schedule due to a slight modification in production recipe.

Nevertheless, discrete models have been used for a wide range of industrial scheduling problems where considerable time intervals are required to obtain an accurate representation of time (Mendez, et al., 2006).

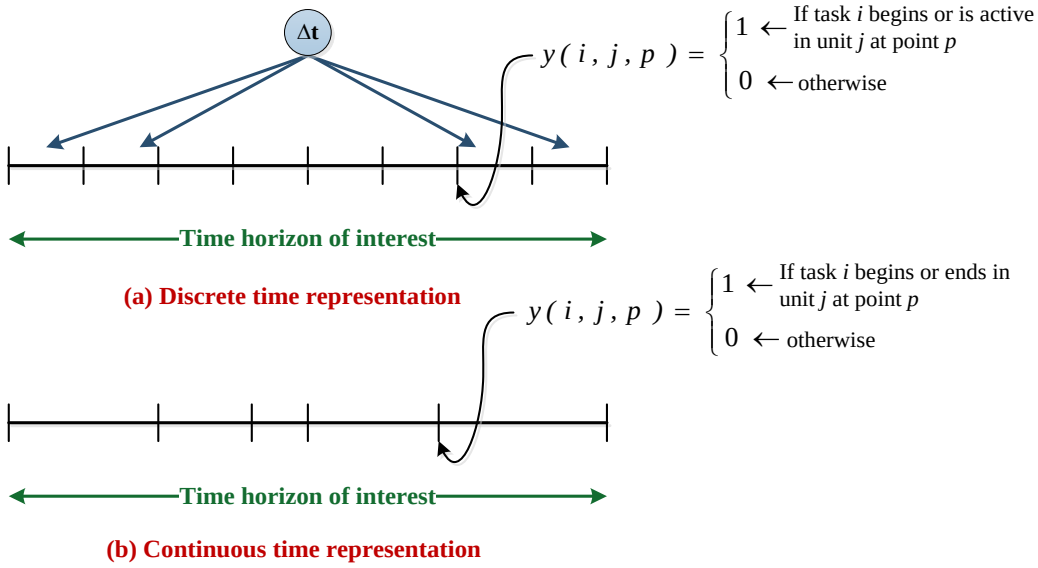


Figure 2.7 *(a) Discrete and (b) Continuous time representation (Majozi, 2010)*

Continuous time approaches were then introduced to improve on the aforementioned shortcomings of discrete formulations. In continuous time approaches, a set of

continuous variables is used to explicitly represent timing decisions which define the exact time at which tasks occur. The formulation becomes flexible in terms of timing decisions by allowing a task to start or end anytime within the given horizon. The resultant time points have proven to be fewer than discrete time formulations and coincide with either the start or the end of a task, as illustrated in Figure 2.7(b) (Schilling & Pantelides, 1996). Continuous time approaches have the advantage of reducing the model size by using fewer time points and decision variables in the scheduling model and it has proven to represent time more accurately (Harjunkoski, et al., 2014). However, the exact number of time points required in continuous formulations is not known beforehand and an iterative procedure is required until no improvement in the objective value is observed.

2.3 Scheduling of batch processes

2.3.1 Definition

Scheduling is a decision-making process that plays an important role in the batch process industry (Pinedo & Chao, 1999). It helps with the improvement of production performance by defining when, where and how a set of products need to be manufactured; given certain requirements in a specific time horizon, a set of limited resources and processing recipes (Mendez, et al., 2006; Floudas & Lin, 2004). There exist three types of scheduling in batch processes i.e. short-term, medium term and long term scheduling. Long-term scheduling deals with a long time horizon and focuses on resources allocation and high-level decisions making such as timing and location of additional facilities. Medium-term scheduling considers medium time horizons and determines detailed production schedule. It can, therefore, result in large-scale problems with significant computational intensity in mathematical programming. Short-term scheduling addresses shorter time horizons that can go up to several hours or days depending on the granularity of the problem. It also focuses

on both resource allocation and determines a detailed sequencing of various operational tasks (Dhamdhere, 2006; Seid, 2013).

Traditionally, the scheduling of a batch process was performed manually by trained individuals. However, it was relatively difficult to accommodate any fast change in the production demand or other economic aspects since rescheduling was required. It was then proved that a good and profitable production schedule that ensures a reduction in environmental load and minimum utilities demand could only be achieved with an optimization support (Harjunkoski, et al., 2014). Hence, the development of mathematical models to optimize batch production schedule has been the subject of many research studies. Various other aspects are considered when performing scheduling of batch processes. These include the representation of the production recipe, the representation of the time dimension, the mapping of events within the time horizon and the storage philosophies for intermediate materials. This section will give a background on mathematical programming and optimization, and a review of existing mathematical formulations for the short-term scheduling of batch processes.

2.3.2 Mathematical modelling and optimisation

Mathematical modelling is a powerful tool capable of describing the interactions between different aspects of a real world scenario through mathematics. It plays a pivotal role in science and engineering by filling the gap between theoretical analysis and experimentation (Quarteroni, 2009). Mathematical models involve a set of mathematical relationships such as equations and inequalities and can be classified as programming models, simulations models, time series model, etc. Programming models are mathematical models that have optimisation as their common feature. Their general structure involves a set of *constraints* (equality and/or inequality constraints) referred to as *process model* and an *objective function* to be maximised or minimised. Optimisation consists of selecting the best possible solution to a problem

from a set of available alternatives. In other words, it aims to find the best value of the objective function given a set of constraints describing a certain process or real-world scenario (Williams, 2013).

(a) Model classification

The classification of programming models is based on the mathematical structure of constraints, the objective function, and the type of variables involved. The two main types of variables found in mathematical programming models are continuous variables and Integer variables. Integer variables can only take integer values while continuous variables are more generic and take any real value. Depending on the structure, a mathematical model can be classified as *Linear Programming (LP), NonLinear Programming (NLP), Integer Programing (IP), Mixed Integer Linear Programming (MILP) and Mixed Integer NonLinear Programming (MINLP)* .

A model is referred to as LP when the objective function and all the constraints involved are linear expressions. Constraints (2.1) to (2.5) give the mathematical structure of a typical example of an LP maximization problem. It consists of one linear function (2.1) to be maximized subject to four linear constraints (2.2) to (2.5) (Williams, 2013).

$$Max \quad f(x_1, x_2) \tag{2.1}$$

$$s.t \quad g(x_1, x_2) \leq a \tag{2.2}$$

$$h(x_1, x_2) \leq b \tag{2.3}$$

$$k(x_1, x_2) \geq c \tag{2.4}$$

$$x_1, x_2 \geq 0 \tag{2.5}$$

The graphical representation of this problem is illustrated in Figure 2.8 where the feasible region is bounded by the above-mentioned constraints. The optimization problem is then reduced to finding the point within the feasible region where the

objective function takes its maximum value. The optimal solution of an *LP* model has been proven to always lie on the boundaries of the feasible region. In the case of this example, the optimal solution was found to be at point A as shown in Figure 2.8 where the objective function took its highest value (Williams, 2013).

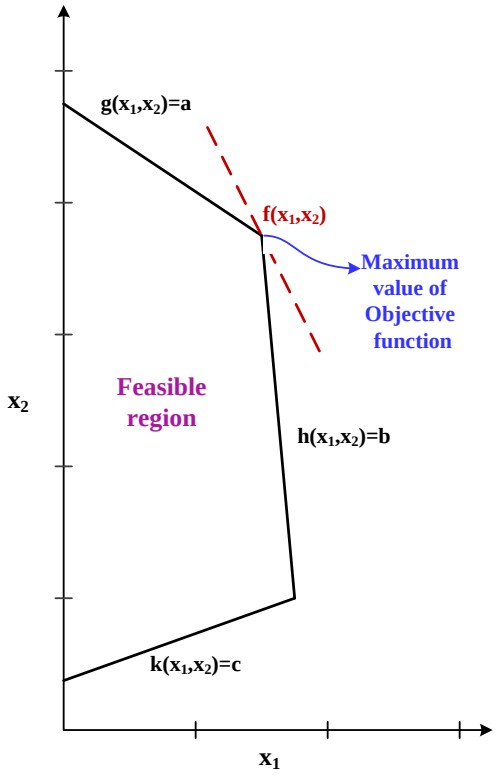


Figure 2.8 *Graphical representation of a LP model* (Williams, 2013)

LP models are the simplest form of mathematical programming models. They are intensively used in the petroleum industry and have various other applications such as transportation problems, portfolio selection in the financial sector, farm management in the agricultural sector and blending problems in the mining industry. However, in instances where more complex problems need to be formulated, LP models are extended to various other types of programming models. In the event where at least one of the constraints, the objective function or both contain nonlinear expressions such as x_2^2 and $x_1 x_2$, the model becomes a NLP problem. A model takes the form of

a *Pure Integer Programming* (PIP) when all the variables it contains are integer variables. The coexistence of both continuous and an integer variable in a mathematical model is referred to as *Mixed Integer programming* (MIP). Depending on whether the constraints and the objective function are linear or nonlinear, MIP models can be further classified as *Mixed Integer Linear Programming* (MILP) and *Mixed Integer Nonlinear Programming* (MINLP) respectively (Williams, 2013).`

2.3.3 Scheduling techniques for batch processes

There exist different techniques that can be used to schedule batch operations occurring within a production facility. The type of technique employed depends on the time representation used in the model and the type of production environment considered. Discrete time models use global time intervals for scheduling in both sequential and network processes. On the other hand, continuous time models represent events using either slot based, event-based or precedence based approaches. Event-based models are used for scheduling problems in network environments and are further divided into global event based and unit-specific event-based models. Slot-based and precedence based models were initially used for sequential processes, but have been further extended to consider network environments (Shaik, et al., 2006).

(a) Global time intervals models

The global time intervals models represent different events, i.e. the starting and finishing time of tasks, occurring in different units by using common time intervals. Figure 2.9 gives an illustration of a global time interval representation for a small batch process with two units processing four and two batches respectively. The length of each interval is predefined in the model since a discrete time representation is used. In these models, tasks are only allowed to begin and end at the interval boundaries which simplify the scheduling problem to an allocation problem (Mendez, et al., 2006).

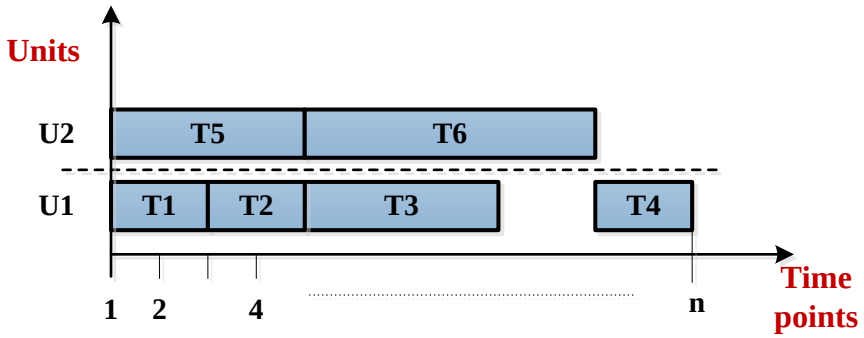


Figure 2.9 *Global time interval models (Harjunkoski, et al., 2014)*

(b) Global and Unit-specific event- based models

The global event-based technique is a generalization of the global time intervals technique. Their similarity relies on the fact that the time intervals are common across all the units. However, in global event based models, each time interval has a variable length which is not known beforehand as shown in Figure 2.10(a). This implies that the duration of each interval is modelled as a decision variable during optimization (Mendez, et al., 2006). The unit specific event based representation, on the other hand, use a variable time grid which is each processing unit. Its uniqueness comes from the fact that it allow the value of a time point to vary from one unit to the other as shown in Figure 2.10(b).

The advantage of global event -based models is the fact that they provide a reference time grid for all units which usually simplify formulation pertaining to the optimization of batch plants. However, it usually requires a larger number of event points compared to unit-specific event based models. In the latter, the use of unit-specific time grids allow some units processing fewer batches to use fewer time points which leads to an overall reduction of time points used in a given formulation.

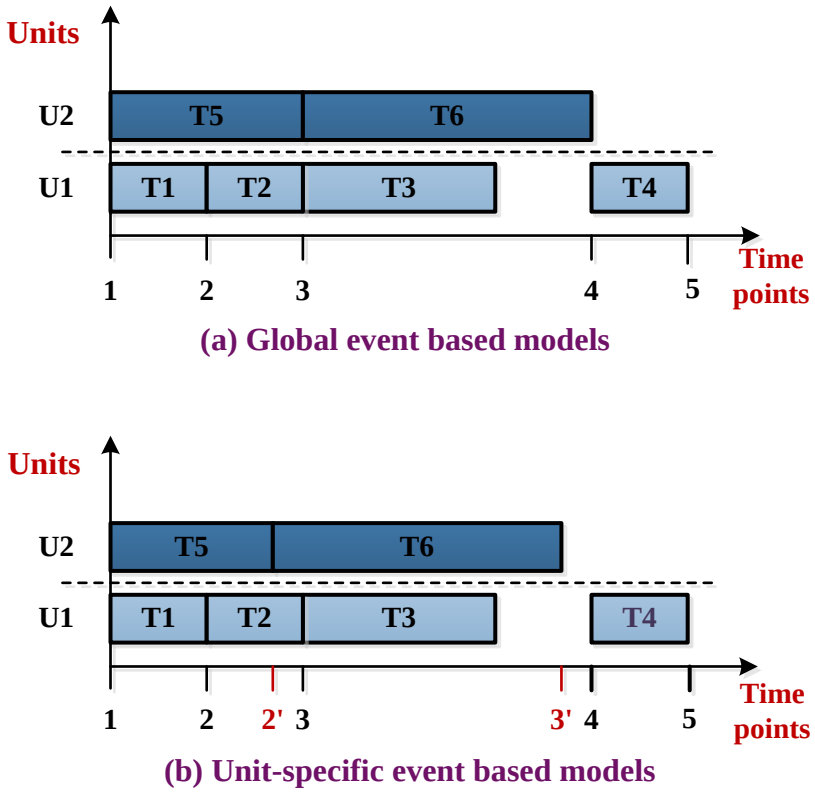
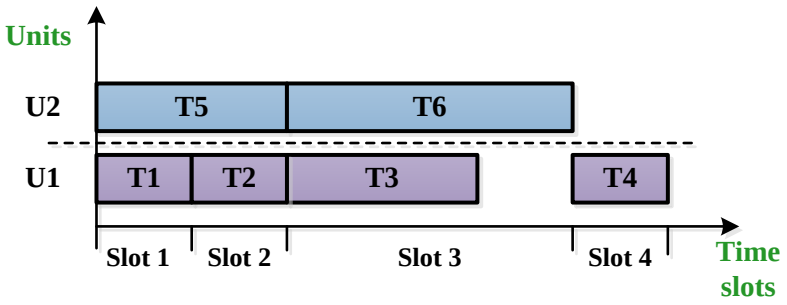


Figure 2.10 *Global event and unit-specific event based models (Harjunkoski, et al., 2014)*

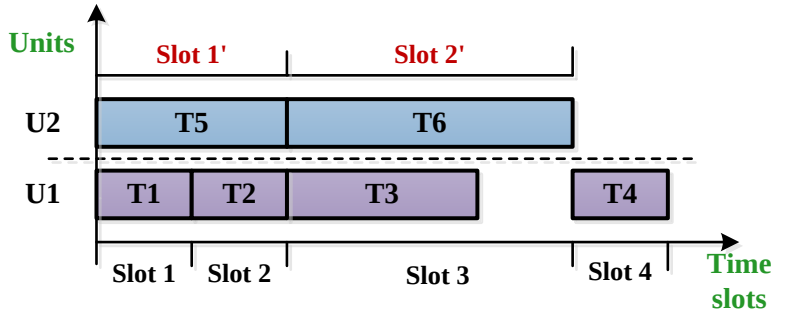
(c) Slot based models

Slot based models use a predefined number of time slots of unknown duration for each processing unit in order to allocate them to different tasks to be performed. These techniques often allow a task to be allocated to more than one slot if the required number of time slots is overestimated. Slot based representations are very similar to event based representations in that they both use time grids to represent tasks and events. They are further subdivided into synchronous (process slots) and asynchronous (unit slots) models. Synchronous models use common slots across all units, as shown in Figure 2.11(a) while asynchronous models use different slots for different units, as illustrated in Figure 2.11(b) (Mendez, et al., 2006). Therefore, due

to the similarity between slot based and event based models, it can be concluded that asynchronuous slot based models use fewer time slots and reduce the size of resultant mathematical formulations.



(a) Slot based models (synchronous)



(b) Slot based models (asynchronous)

Figure 2.11 *Synchronous and asynchronous slot based representations (Harjunkoski, et al., 2014)*

(d) Precedence- based techniques

Precedence-based techniques are batch oriented formulations aiming to determine the optimal sequence of jobs in each processing unit present within a batch plant. These techniques do not use time grids uniques the other aformentioned tecniques. They are divided into immediate precedence and general precedence based techniques.

Immediate precedence techniquess only consider the immediate predecessor of a batch whilst general precedence based techniques consider any predecessor of a particular batch in a unit. For instance, as shown in Figure 2.12, the immediate predecessor of task T4 which is performed in unit U1 is task T3 whilst tasks T1, T2 and T3 are all considered as predecessors of task T4 in general precedence based formulations. General precedence based techniques have the advantage of using a single sequencing variable to allocate a pair of batch tasks to the same shared resource such as a processing unit. Therefore, they result in smaller formulations when compared to immediate precedence based techinques. The major weakness of precedence based techniquess is the increase in the number of sequencing variables with increasing number of batches to be scheduled. Consequently, this can result in very large scale models for real case scenarios (Mendez, et al., 2006).

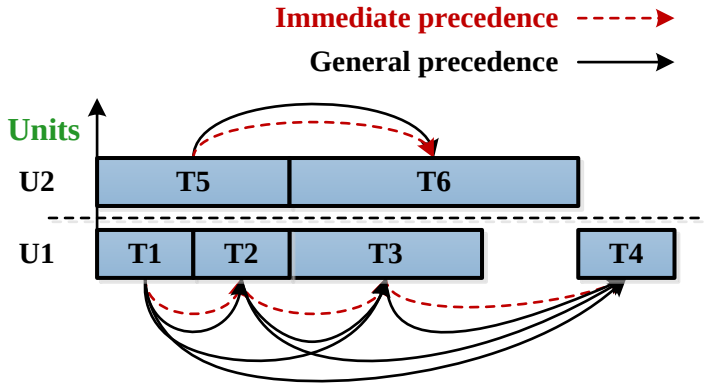


Figure 2.12 *Precedence-based techniques for event representation (Harjunkoski, et al., 2014)*

2.3.4 Review of short-term scheduling models for batch processes

Kondili et al. (1993) developed the earliest model for the short-term scheduling of multipurpose batch processes. Their model used the STN for recipe representation, a discrete time representation where a single grid is used for the mapping of tasks in all

existing units as shown in Figure 2.9. A three-index binary variable W_{ijt} was used to denote the start of the processing of task i by unit j at the beginning of time period t . Allocation constraints were used to ensure that a unit only performed one task at a time while material balances captured the net increase or decrease in inventories in storage tanks. The formulation allowed all type of intermediate storage policies to exist within the process. Many other aspects of batch process scheduling were considered in this formulation as listed below.

- The temporary unavailability of resources during certain time periods. This may be due to the need for maintenance or breakdown during plant operation.
- The limited availability of utilities and discrete resources such as manpower.
- Sequence-dependent cleaning which entails that the extent of cleaning can depend on the sequence of tasks in that units.
- Frequency-dependent cleaning which considers cases where the need for cleaning a unit depends on the frequency of its utilization

The model aimed to maximize the profit of the plant and the objective function considered the production revenue, the cost of feedstocks, the running costs of storage tanks and the cost of utilities. However, due to the discrete time representation, the formulation led to very large MILP scheduling problems.

Schilling and Pantelides (1996) then presented a synchronous slot based scheduling formulation using the RTN framework of Pantelides (1994). The formulation forced the starting and finishing time of all tasks to coincide with time points on the time grid. In other words, the length of a time slot was modeled to be equal to the duration of a specific task. A variable processing time which depends on the size of the batch was considered for all tasks. The objective of their formulation was to maximize the net accumulation of resources minus the cost of performing various tasks. The authors addressed the issue of large integrality gaps in continuous time formulations which increase their computational burden by developing a branch and bound

algorithm where both continuous and integer variables are branched and tighter bounds are imposed on slot durations.

Zhang and Sargent (1996) then developed a global event based models using a RTN representation to improve the discrete time RTN model of Pantelides (1994). In this formulation, A batch task was modelled to start at an event time point while consuming and generating a set of resources at the start and end of its execution respectively. The formulation aimed to maximize the plant profit and yielded a large nonconvex MINLP for which the author addressed the computational difficulties associated with the nature of the model. The model was then simplified by reducing the number of nonlinear terms and fixing the production recipe, i.e. fixing the processing time of batch operations. This then resulted in a drastic reduction in model size and CPU time.

Cerda et al. (1997) developed the first precedence based MILP formulation for the scheduling of a single stage multiproduct batch plant with parallel units. The concept of immediate predecessor and successor of a batch was introduced to effectively handle sequence-dependent changeovers between different batches in a unit. The formulation aimed to determine the optimum sequence of jobs in processing units. The model assumed that the size of each batch was fixed to the maximum capacity of the unit performing the job. Different batches producing the same order were modeled to be performed in the same unit. The objective functions considered were the minimization of the overall tardiness, the makespan and the number of tardy orders.

Ierapetritou and Floudas (1998) introduced the concept of unit specific event-based modelling to address the problems associated with global event-based and discrete models. Their MILP formulation adopted a STN for batch recipe representation. A concept of decoupling task events from unit events was introduced in an effort to reduce the size and computational burden of previous continuous time formulations.

The binary variable W_{ijt} commonly used in previous STN formulation led to large numbers of binary variables of dimension *i* x *j* x *t*. The authors replaced it with two binary variables *wv(i,n)* and *yv(j,n)* where *wv(i,n)* assigns the beginning of task *i* to time point *n* and *yv(j,n)* denotes the beginning of the utilization of unit *j* at time point *n*. e allocation constraint was formulated by ensuring that only one task is assigned to a unit at any given point in time as described by Equation (2.6) below.

$$\sum_{i \in I_j} wv(i,n) = yv(i,n), \forall j \in J, n \in N \tag{2.6}$$

The authors also demonstrated that for batch processes where a unit is only allowed to process one task, Equation (2.6) can be reduced to *wv(i,n)=yv(i,n)*. This allows the elimination of the *yv(i,n)* binary variable and Constraint (2.6), resulting in a drastic reduction of the model size. Time sequencing constraints for tasks occurring in the same and/or different units were also introduced and the events were modelled as shown in Figure 2.10(b). Moreover, nonlinear terms usually found in previous continuous time formulations were avoided, rendering the formulation simpler and easier to solve.

Majozi and Zhu (2001) introduced the SSN representation and presented a scheduling formulation attempting to improve the existing unit-specific event-based models. Their formulation only used a binary variable *y(s,p)* to denote the use of a state *s* at a given time point *p* which inherently implied that the unit is starting to process a certain task is being processed in a unit at a given point in time. The authors considered the case where the duration of a task can vary depending on its batch size. Overall, Their formulation was able to further reduce the number of binary variables used to model a scheduling problem. Consequently, the computational intensity of unit specific event based models was alleviated, enabling scheduling problems to be solved to optimality. An aggregation model was also presented whereby processing units performing similar tasks in a particular processing stage are modelled as a single

unit. This was performed to achieve a further reduction in the size of mathematical models aiming to schedule multi-stage batch plants with an in-phase operation of processes.

Maravelias and Grossman (2003) presented a global event based formulation for the scheduling of multipurpose batch plants using a STN framework. The authors considered both a fixed an a variable processing time of tasks and used the concept of task decoupling proposed by Ierapetritou and Floudas (1998). Various storage policies including the UIS, FIS, NIS and ZW policies were explored. A mixed global event representation was introduced wherein tasks producing at least one unstable state and requiring a ZW policy were modelled to start and end at interval boundaries. All other tasks were allowed to end at any time within a given time interval. The global alignment of events allowed the formulation to have less sequencing constraints compared to unit specific event-based approaches. The authors also proposed a hybrid Generalized Disjunctive/Mixed Integer Programming technique to reduce the CPU time of global event-based models.

Sundaramoorthy and Karimi (2005) proposed a simple synchronous slot based approach for the short-term scheduling of multipurpose batch plants. The original three-index binary assignment variable proposed by Kondili et al. (1993) was used instead of the decoupling method of Ierapetritou and Floudas (1998). The authors demonstrated that, for a set of unit J_i performing task i, both approaches led to the same number of binary variables per event point which is equal to the sum of cardinalities of set J_i for all tasks i. Their formulation allowed tasks to span over multiples slots by defining a binary variable Y_{ijk} and three 0-1 continuous variables Z_{jk}, y_{ijk} and YE_{ijk} as follows.

$$Y_{ijk} = \begin{cases} 1 \rightarrow & \textit{if unit j begins task i at time } T_k \\ 0 \rightarrow & \textit{Otherwise} \end{cases} \tag{2.7}$$

$$Z_{jk} = \begin{cases} 1 \rightarrow & \textit{if unit j begins a task at time } T_k \\ 0 \rightarrow & \textit{Otherwise} \end{cases} \quad (2.8)$$

$$y_{ijk} = \begin{cases} 1 \rightarrow & \textit{if unit j is continuing to perform task i at time } T_k \\ 0 \rightarrow & \textit{Otherwise} \end{cases} \quad (2.9)$$

$$YE_{ijk} = \begin{cases} 1 \rightarrow & \textit{if unit j end task i releases its batch at time } T_k \\ 0 \rightarrow & \textit{Otherwise} \end{cases} \quad (2.10)$$

Logical constraints where used to ensure that the 0-1 continuous variables behave like binary variables and model the status of a unit at a specific time point T_k. A slot *k* was modelled to have a duration SL_k, starting from T_{k-1} to T_k. The material balance consisted of modelling the variation of batch size as materials enter or leave the unit. Material inventory at each processing stage was ensured by performing a material balance on storage tanks at each time point by assuming that tasks withdraw and transfer materials from and to storage at the beginning and end of their operation. The transfer time was assumed to be included in the processing time as assumed in previous formulations. Both profit maximisation and makespan minimisation were considered as objectives of batch production schedule optimisation.

Shaik and Floudas (2008) then first explored the use of RTN representation in unit specific event-based models. A binary variable *w(i,n)* was used to assign a given task *i* at the beginning of time point *n*. The formulation consisted of resource balances, capacity, and sequencing constraints. The authors included sequencing constraints to adequately cater for the FIS policy as opposed to simply using an upper bound on the amount of materials stored at each time point. The latter, adopted by the work of Ierapetritou and Floudas (1998) and Majozi and Zhu (2001), can lead to infeasible

schedules which violate storage constraints. This is mainly due to the fact that, in unit specific event based, time points have time values differing from one unit to the other. The FIS sequencing constraints of Shaik and Floudas (2008) were modelled as follows.

$$T^s(i,n+1) \leq T^s(i',n) + \alpha_{i'} w(i',n) + \beta_{i'} b(i',n) + H(2 - w(i',n) - w(i,n+1)) \quad (2.11)$$

$$T^s(i,n+1) \geq T^s(i',n) + \alpha_{i'} w(i',n) + \beta_{i'} b(i',n) - H(1 - w(i',n)) \quad (2.12)$$

$$T^s(i,n) \leq T^s(i',n) + \alpha_{i'} w(i',n) + \beta_{i'} b(i',n) - H(1 - w(i',n)) \quad (2.13)$$

Constraints (2.11) and (2.12) together enforced a zero wait policy between two consecutive tasks *i* and *i'*, respectively producing and consuming a resource with limited intermediate storage. $T^s(i,n)$ denotes the starting time of task *i* at a given time point *n*. In doing so, treating storage as separate tasks was avoided. Constraint (2.13) then ensures that the starting time of the task consuming an intermediate state with finite storage should start before the end time of its producing task if both tasks occur at the same event point *n*.

Ferrer-Nadal et al. (2008) later addressed the assumption of lumping the transfer time of intermediate materials between two units into the processing time of tasks involved in their production. This assumption is usually based on the negligible duration of the transfer time as compared to the processing time of a task. The authors proposed a general precedence based model for multistage batch processes which involves synchronization of processing units during transfer time. This entailed that the units supplying and receiving intermediate materials could not process any task during the transfer time in order to obtain a feasible plant schedule. The objective function of the optimization model was the minimization of the makespan.

Li and Floudas (2010) addressed the major issue of time point determination associated with continuous time formulations. They developed a framework to determine the optimum number of time points for scheduling models aiming to maximize profit or minimize makespan. Their technique was based on a unit specific event based model proposed by Shaik and Floudas (2009) which relied on a three index binary variable *w(i,n',n)* defined as follows.

$$w(i,n',n) = \begin{cases} 1 \rightarrow & \textit{Task i starts at time point n' and ends at time point n} \\ 0 \rightarrow & \textit{Otherwise} \end{cases} \quad (2.14)$$

This allowed a particular task to span over multiple time points between *n'* and *n*. The model was extended by Li and Floudas (2010) to consider a wider range of storage philosophies, i.e. UW, ZW, FW, FIS and UIS, and their implication in the time point determination framework. The proposed determination framework is given in Figure 2.13 where CIS, N_{max} , N_{min}, and N_{opt} stand for critical intermediate states, maximum, minimum and optimum number of event points respectively. A critical intermediate state (CIS) in this case was defined as the intermediate material that has the highest effect on the objective value when solving the scheduling model with relaxed sequencing constraints. An iterative procedure was used to determine the maximum number of time points N_{max} and the CIS(s). The main issue with iterations is the drastic increase in the time required to get the optimum plant schedule as the size of the model increases. It is worth pointing out that for a makespan minimization problem, the framework suggests that a feasible makespan should be determined prior to the determination of the CIS as shown in Figure 2.13(b). This was obtained by solving the scheduling model using the minimum number of time points while restricting the CPU time and ensuring that the product demand was not exceeded.

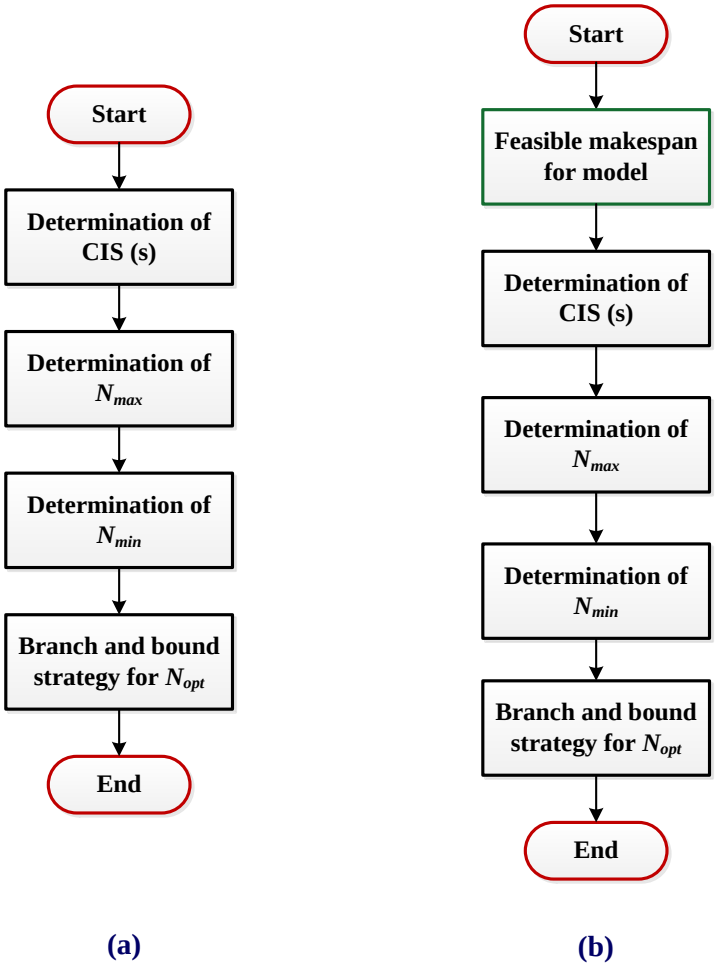


Figure 2.13 *Optimal event determination framework for (a) profit maximization and (b) makespan minimization problems (Li & Floudas, 2010)*

Susarla et al. (2010) proposed an asynchronous slot based model for the scheduling of multipurpose batch plants. A task was allowed to span consecutive time using a binary and three 0-1 continuous variables as proposed by Sundaramoorthy and Karimi (2005). The formulation also catered for non-simultaneous transfer of materials from storage units to processing units. This was modelled using two variables δ_{jk} and θ_{jk} which represent the time period for which a unit j is idle at the beginning and the end of slot k respectively. Therefore, transfer of materials between storage tanks and processing units were allowed to occur non-simultaneously within

periods δ_{jk} and θ_{jk} respectively. This implied that a start could then start and end anytime within a slot. The formulation accounted for various storage configurations, i.e. FIS, UIS, NIS, and different wait policies for intermediate materials, i.e. UW, FW, and ZW policies. Different possible objective functions were considered for schedule optimization and this included revenue maximization, makespan minimization and net profit maximization. The net profit in this formulation took into account the cost associated with all produced materials rather than just sellable products.

Seid and Majozi (2012a) then presented a novel technique for the scheduling of multipurpose batch plants based on an SSN framework. The authors improved on the formulation of Majozi and Zhu (2001) by reducing the number of time points and states used to model tasks and events. Their formulation used a state to represent a task to be processed instead of representing an input or output material as proposed by Majozi and Zhu (2001). The reduction in the number of time points was achieved by allowing the starting and finishing time of a task to occur at the boundaries of a given slot *p* as opposed to using two distinct time points. The difference between both models is shown in Figure 2.14. This resulted in a considerable reduction in the model size as compared to previous formulations. The authors also proposed a flexible method for handling intermediate materials with FIS constraints through the use of Constraints (2.15) and (2.16) below.

$$\sum_{s_j^{in} \in S_{in,j}^{sp}} \rho_{s_j^{in}}^{sp} m_u\left(s_j^{in}, p-1\right) + q_s(s, p-1) \leq QS^U + \sum_{j \in J_s} V_j^U (1 - x(s, p)) \tag{2.15}$$

$$t_u\left(s_{j'}^{in}, p\right) \leq t_p\left(s_j^{in}, p-1\right) + H\left(2 - y\left(s_{j'}^{in}, p\right) - y\left(s_j^{in}, p-1\right)\right) + H\left(x(s, p)\right) \tag{2.16}$$

Constraint (2.15) ensures that the amount of intermediate state stored at any point in time does not exceed the available storage capacity. The binary variable *x(s,p)* indicates the availability (*x(s,p)*=1) or absence of storage (*x(s,p)*=0) for intermediate sate s at time slot *p*. Constraint (2.16) then states that the finishing time of the

producing task should coincide with the starting time of the task consuming state *s* provided that no storage is available for this state, i.e. $x(s,p)=0$. This constraint is relaxed if there is an available storage for intermediate state *s*, i.e. $x(s,p)=1$. The PIS policy for materials having a finite intermediate storage capacity was explored. The unit producing such materials was allowed to be used for its temporary storage provided that it is not assigned to any other task during that time period.

Seid and Majozi (2012b) then used the scheduling model of Seid and Majozi (2012a) to develop a novel approach to predict the optimum number of time points. The proposed approach is shown in Figure 2.15 Their prediction was based on the number of instances a critical unit is used within a given horizon. This was obtained by solving the proposed LP max and LP min models which were based on the analysis of the production recipe. Their methodology did not require iterations at any step of the time point determination framework as opposed to the work of Li and Floudas (2010).

Shaik and Vooradi (2013) then presented a novel unit specific event approach for the unified treatment of all resources aiming to maximize the plant profit. The resources considered included material states, storage tasks, cooling water, low-pressure steam (LPS), high-pressure steam (HPS), and discrete resources such as manpower. This approach unified STN and RTN based formulations with the difference residing in the way equipment resources are handled. Tasks were allowed to span multiple event points n using a binary variable $w(i,n,n')$ as proposed by Shaik and Floudas (2009). A new feature was introduced whereby the number of events a task is allowed to span vary from one task to the other. The sttorage of materials were modelled as separate tasks in order to avoid aggregations of storage tanks and sharing of storage tanks was considered. The formulation also allowed different tasks using the same utility to occur at different point in time to improve the global alignment philosophy proposed by Shaik and Floudas. Satisfaction constraints were used to cater for scheduling problems with multiple product orders.

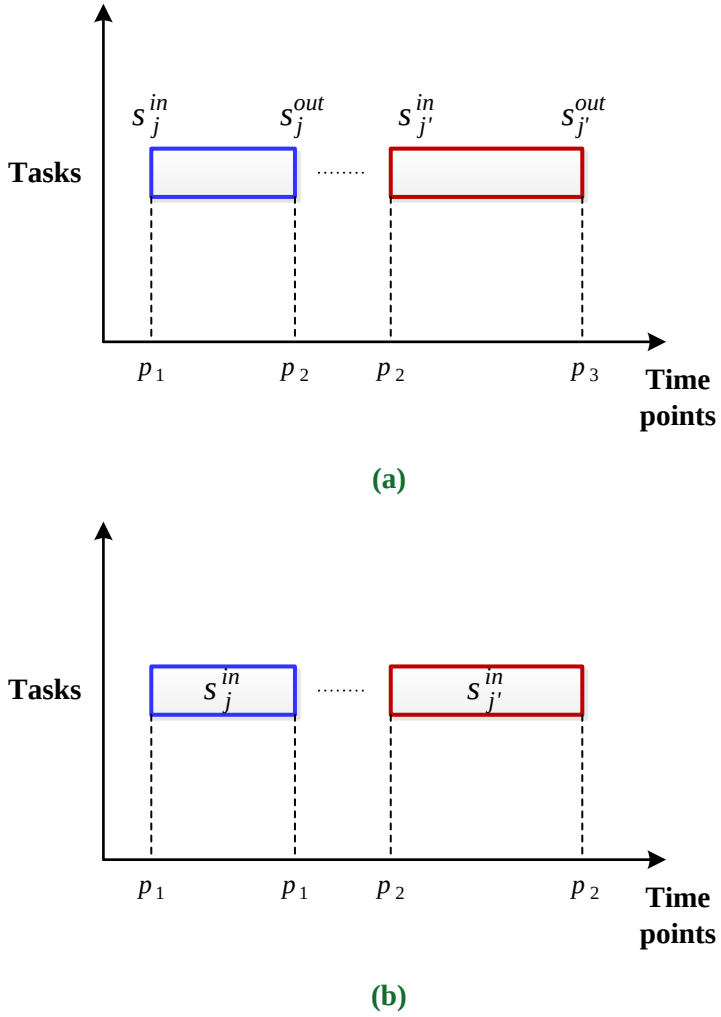


Figure 2.14 *Scheduling technique of (a) Majozi and Zhu (2001) and (b) Seid and Majozi (2012b)*

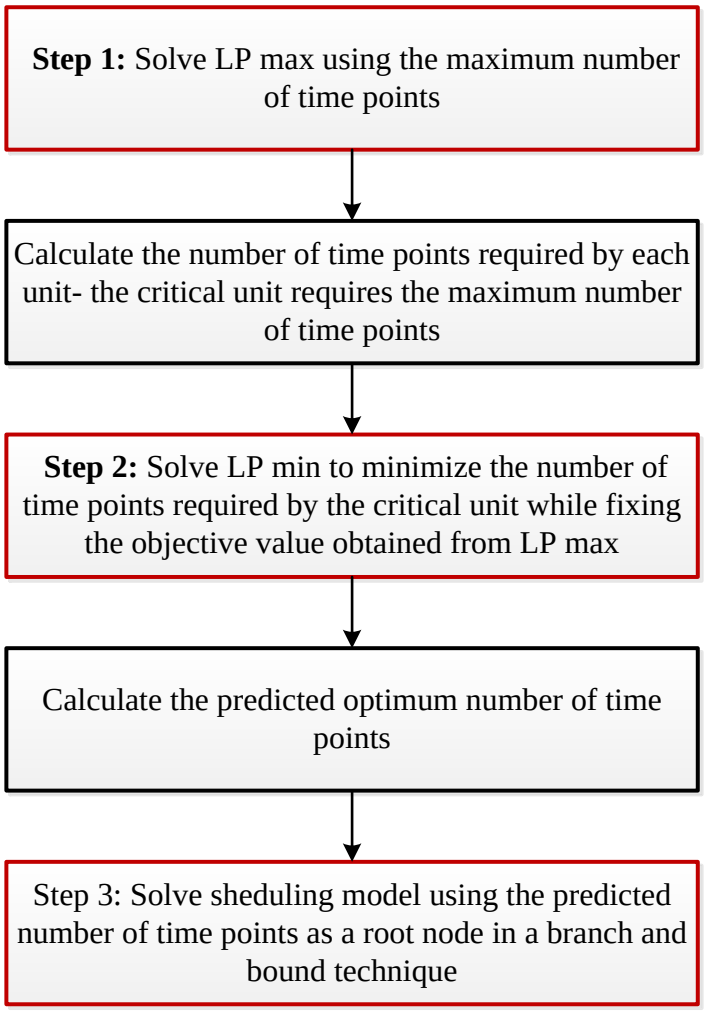


Figure 2.15 *Procedure of Seid and Majozi (2012b) to predicting the optimum number of time points*

2.4 Wastewater minimisation in batch plants

The minimisation of freshwater use in batch plants is usually achieved by implementing process integration opportunities. El-Hawagi (1998) defines process integration as a "holistic approach to process design and operation which emphasizes the unity of process units and objectives". Its merit relies on its ability to integrate various objectives such as environmental problems (e.g. pollution) with other process

objectives like profitability and utility reduction. The application of process integration techniques in batch processes has been the subject of many research studies. These techniques include direct reuse, indirect reuse, and regeneration reuse. Direct reuse consists of transferring water between two different units provided the finishing time of the unit discharging water and starting time of the task receiving water coincide as shown in Figure 2.16(a). Indirect reuse involves the usage of storage tanks to allow water to be stored for later reuse. In this case, the time dimension is relaxed in the sense that the starting and finishing times of water using operations do not coincide as shown in Figure 2.16(b). Regeneration reuse consists of partially treating highly contaminated wastewater to facilitate its reuse for further reduction in freshwater intake. Depending on the operation mode of the regeneration process, one or two storage tanks can be used as shown in Figure 2.16(c). A single storage and feeding tank is used for the batch operation of the regenerator while two or multiple storage tanks are required for continuous or semi-continuous operation of the regenerator.

Existing research studies for wastewater minimisation in batch processes are broadly grouped into fixed schedule and flexible schedule techniques. Fixed schedule techniques consider that the schedule of the plant is known prior to applying any water integration techniques. Flexible schedule techniques, on the other hand, allow the scheduling of batch operations to be performed simultaneously with the synthesis of the batch water network for wastewater minimization. Fixed scheduling techniques usually simplify the optimization problem to only a water allocation problem while flexible schedule technique enables a schedule yielding minimum consumption of freshwater to be obtained. The latter then guarantees more water reuse opportunities to be found which entails a possibility for more reduction in wastewater generation.

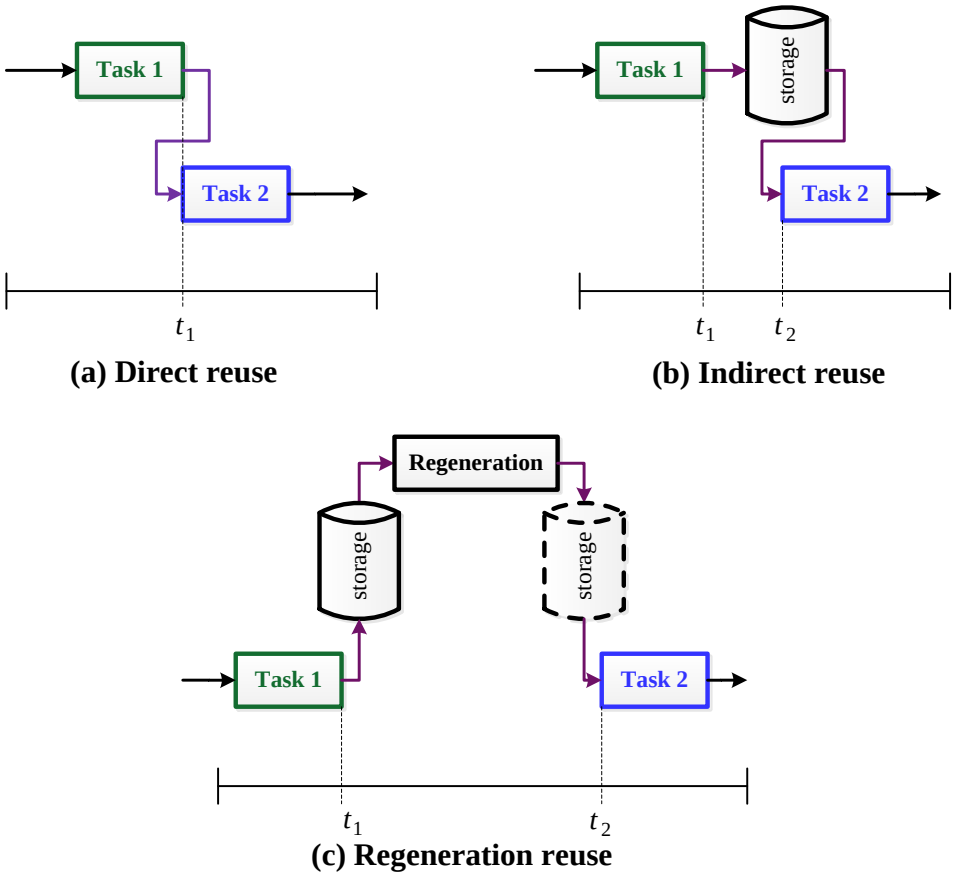


Figure 2.16 *Water integration techniques for in batch processes*

2.4.1 Fixed schedule techniques

Fixed schedule techniques are classified by the adopted optimisation approach. Optimisation techniques in place include insight based techniques, mathematical modelling techniques, and hybrid techniques. Insight based techniques allow the engineer to visually target minimum freshwater using graphs and/or algebraic concepts and readily design the resultant integrated water network. However, Their main limitation is their inability to adequately handle multidimensional optimisation problems such as wastewater minimisation with flexible schedule and multiple contaminants. Mathematical modelling techniques involve the development of

programming models in which minimum freshwater use and network design are simultaneously yielded by the model. While this approach is not limited in dimension, computational difficulties such as high CPU time may arise when solving complex optimization problems. Hybrid techniques then combine both insight-based concepts and mathematical modelling with the aim of benefiting from both techniques. Contributions for wastewater minimisation made under each category of optimization techniques are thoroughly explored in this section.

(a) Insight-based techniques

Wang and Smith (1995) were the first to develop a technique for wastewater minimisation in batch processes. The authors modified the water pinch technique of Wang and Smith (1994) to consider time as a primary constraint and concentration driving force as a secondary constraint. This entailed dividing a specific problem into concentration intervals and time subintervals, grouping existing processes in each concentration interval and reusing effluents from one concentration interval to the subsequent one. Freshwater was fed at intervals were no effluent was available for reuse and as a top up to meet the water requirement in each concentration intervals. Figure 2.17 shows graphs of water targeting at two consecutive intervals whereby freshwater is supplied to processes existing in the first interval and effluents from the first interval are cascaded to the second interval for reuse. The cascaded water is represented in Figure 2.17 as "water available for reuse". Once the targeting procedure was performed in all existing concentration intervals, the integrated batch water network was then designed. However, their resultant network could not be implemented in batch processes for it allowed the reuse of water to occur between operations with overlapping time intervals. The network also suggested the usage of storage which was not practically needed because timing constraints were satisfied for direct reuse to occur. Furthermore, this technique can only be applied to mass transfer based operations, i.e. operations where water is used as a lean stream for the extraction and removal of contaminants.

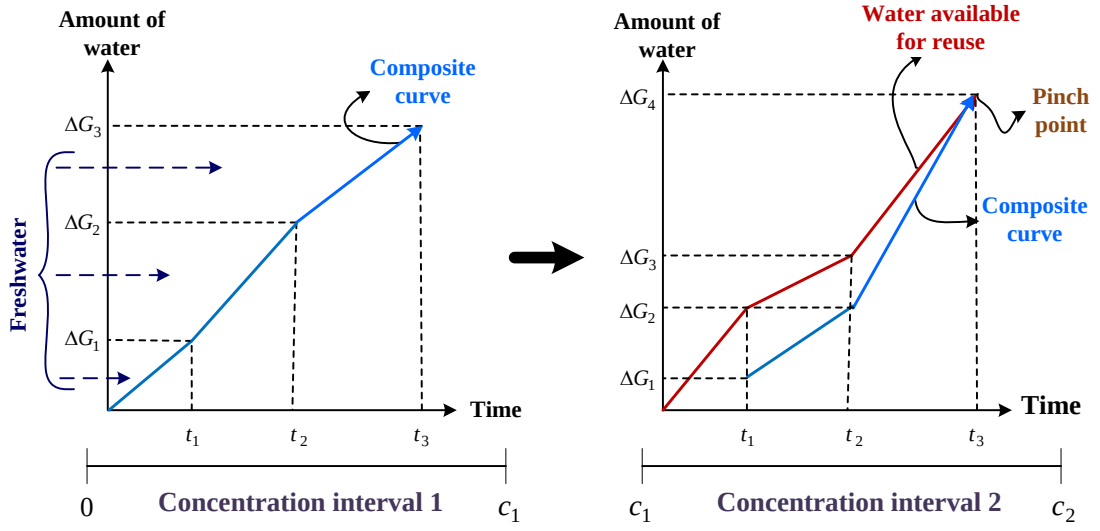
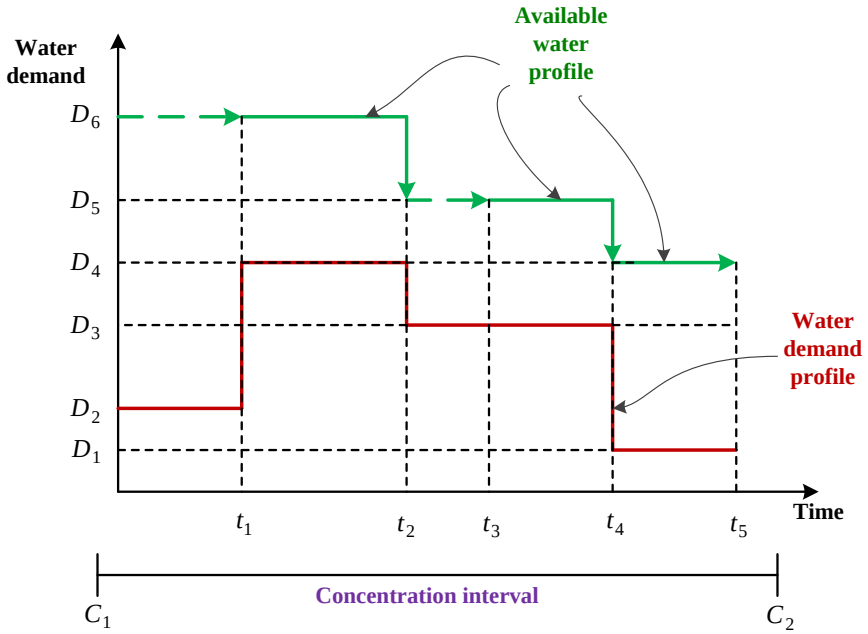


Figure 2.17 *Graphical technique of Wang and Smith (1995) for water targeting in batch processes*

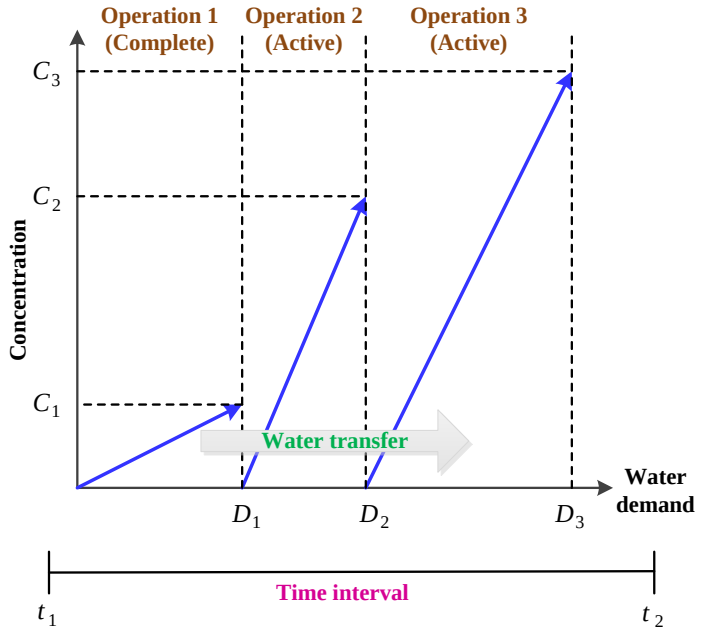
Foo et al. (2005) proposed a numerical procedure for the synthesis of maximum water recovery network for batch processes with a single key contaminant. The technique involved two stages whereby the first stage consisted of determining the minimum freshwater and wastewater targets using the *time-dependent water cascade analysis* (WCA). The second stage then focused on designing the water network based on the targeted utility consumption. Their work was adapted from the two-stage procedure of Foo et al. (2004; 2005a) for the synthesis of batch mass exchange networks and the WCA technique of Manan et al. (2004) targeting minimum freshwater flowrate in continuous processes. This technique employed classification of a process into a source and/or demand introduced by Dhole et al. (1996) to allow for different types of processes to be included while developing strategies for the optimization of water use. This enables WCA to cater for both mass-transfer and non-mass transfer based operations in both batch and semi-continuous processes.

The time-dependent WCA technique is performed in a tabular form and can be briefly explained as follows. In the first column, all existing contaminant concentration levels expressed in ppm are arranged in ascending order. In the next column, the existing concentration levels are expressed in terms of water purity with freshwater being set at a concentration of one million ppm. Next, all sources and demands are tabulated at their corresponding purity level and within the time interval in which they exist. The WCA of Manan et al. (2004) is then performed at each time interval to obtain the minimum freshwater and wastewater target by exploring direct reuse of water. The minimum freshwater and wastewater targets across all intervals add up to the optimum freshwater use and wastewater generation of a given batch process. When indirect reuse is explored, the targeting is performed once by adding sources and demands at each purity level across time intervals. However, mixing of sources of different purities in the same storage tank is not allowed and this can lead to a large number of storage tanks when many sources of different qualities require storage.

Majozi et al. (2006) address the drawbacks of Wang and Smith (1995) formulation by presenting a new graphical technique for wastewater minimisation in batch processes. The technique considered cases where time and concentration are interchangeably treated as primary constraints as shown in Figure 2.18. When time is treated as a primary constraint, a plot of water demand versus time is used to find possible reuse opportunities across concentration intervals. This is illustrated in Figure 2.18(a), where water demand profile and available water cascade from previous concentration intervals are represented. Figure 2.18(b) then shows a graph of concentration versus water demand where processes are represented using diagonal lines with reuse of water only allowed between completed and starting operations. The technique also considered the use of dedicated storage vessels and processing units as potential storage tanks to override time and increase water reuse opportunities in both state operations. Both single and cyclic batch operations were addressed in this formulation. However, this technique was limited to mass transfer operations.



(a) Time - primary constraint



(b) Concentration - primary constraint

Figure 2.18 *Graphical techniques of Majozi et al. (2006) with (a) time and (b) concentrations treated as primary constraints.*

Liu et al. (2007) then presented a concentration interval analysis (CIA) technique for the synthesis of water utilization network in discontinuous processes. The algebraic technique consisted of constructing a time-dependent concentration interval table where time intervals were defined as the duration of different operations while certain operations could occur at different intervals. Similar to the time-dependent WCA, the minimum water usage was first determined for each time interval and then effluents from one interval were reused in the subsequent interval using a storage vessel to override time. The network design was performed after the water targeting procedure and the resultant network was compared to the one obtained by Wang and Smith (1995) for the same plant. Although the formulation provided a better network in terms of the number of storage tank used, it had the limitation of being more suitable for semi-continuous processes rather than truly batch processes.

Chen and Lee (2008) presented a graphical technique for the design and synthesis of a batch water network involving different types of water using operations. A quantity-time graphical representation was introduced in this formulation as shown in Figure 2.19. This representation clearly maps all water sources and demands available within a batch plant which then allowed for the optimum utility consumption and network structure to be determined simultaneously. The technique also adopted the source-demand representation to cater for mass transfer and non-mass transfer based operations in both batch and semi-batch operation modes. The utility targeting and network design were achieved by first identifying all possible water reuse and recycling opportunities with a minimum number of storage tanks that lead to a practically feasible water network configuration. Similar to the work of Foo et al. (2005), this technique did not allow the mixture of different water sources with different contaminant levels in one storage tank. Moreover, the technique considered both single and cyclic batch operation.

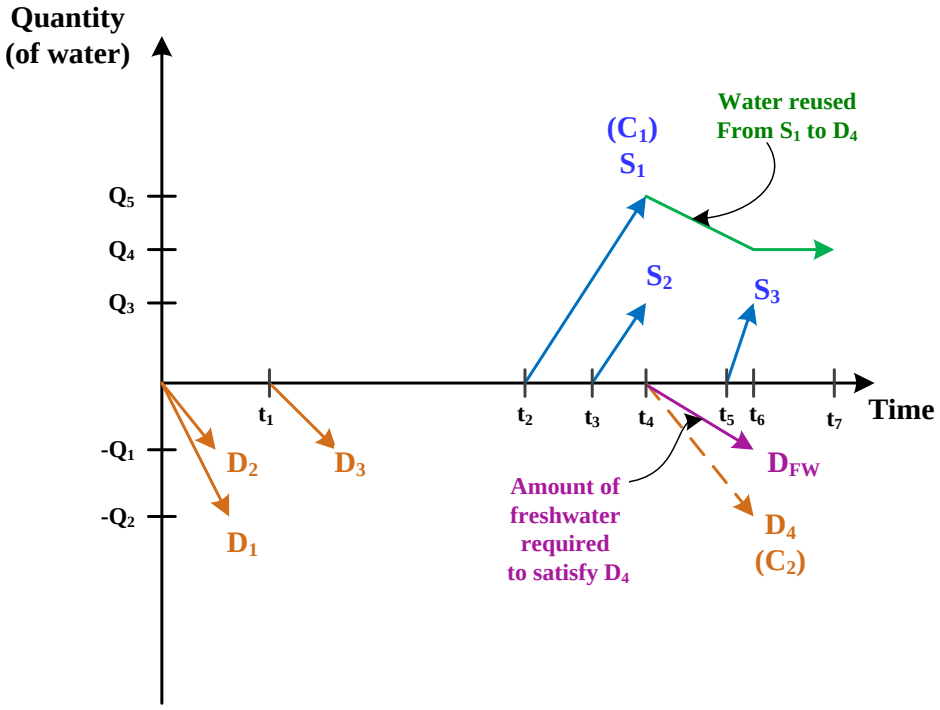


Figure 2.19 *Graphical technique of Chen and Lee (2008)*

Chaturvedi and Bandyopadhyay (2012) proposed an algebraic methodology for wastewater minimisation in both batch and semi-continuous processes. The formulation considered fixed flowrate operations with a single contaminant and known starting and finishing time. The targeting procedure started by considering a single batch process with two time intervals. Next, a three-time intervals batch process was integrated leading to a targeting technique for a batch process with *N* intervals. Using a set of mathematical concepts, a targeting algorithm for both single and cycling batch was established. For a single batch, the procedure consisted of firstly dividing the time horizon into time intervals such that their boundaries coincide with sources and/or demands. The integration was performed in the first interval to achieve minimum waste generation and effluents from the first interval were then used as a source in the next interval. The procedure was carried on to the last time interval. For cyclic batch, the targeting procedure was performed

irrespective of the sequence of intervals by using a continuous process approach. The authors later extended the formulation to batch processes with multiple freshwater sources having different qualities (Chaturvedi & Bandyopadhyay, 2013).

(b) Mathematical modelling techniques

The work of Almato et al. (1999) is among the earliest efforts made toward the development of a mathematical technique for the optimization of water use in batch processes with a fixed production schedule. The NLP formulation consisted of synthesizing a water network with minimum cost using a stream- tank assignment method. The superstructure was made of a set of storage tanks in place to facilitate indirect reuse of effluents from one unit to the other. The optimization problem then consisted of finding the optimum interconnections between units performing batch tasks and storage tanks while determining the quantity and quality of water carried by each pipe. The objective function accounted for freshwater cost, the cost of hot and cold utilities needed to reach the targeted temperature of water streams, and the costs associated with piping and storage.

Kim and Smith (2004) then presented a mathematical formulation for minimization of water use by discontinuous processes. The technique explored both direct and indirect water reuse within a plant. The authors adopted the concept developed by Wang and Smith (1995) which entails splitting an interval at which a task occurs into subinterval to allows more water reuse opportunities to be found. However, by the definition of a batch process operation, materials can only be fed to or discharged from a unit at the beginning or the end of a specific process. Hence this formulated was more suited for semi-continuous processes The objective function consists of the minimization of annualized cost of the water network which includes the cost of freshwater, cost of storage and the piping and interconnection costs. Majozi (2005a) proposed an MILP formulation for wastewater minimization in multipurpose batch plants which considered a single key contaminant. Minimum water usage was

achieved by fixing the contaminant concentration of outlet streams from each unit to its maximum allowable value and searching direct reuse and recycle opportunities between operations.

Chang and Li (2006) designed a water equalization system of buffer tanks in order to achieve the desired flow and concentration of wastewater streams entering the wastewater treatment system. The formulation used a discrete time representation to map operations with predefined starting and finishing time. The number and type of treatments units were stated to be dependent on the type and number of contaminants present in the wastewater streams. However, no information related to the type of treatments units were given for the presented case studies. Furthermore, batch operations were only modelled as sources of wastewater and no reuse was explored. Li and Chang (2006) extended this formulation to consider the use of buffer tanks to facilitate indirect reuse of water by modelling batch operations as both wastewater sources and sinks. Liu et al. (2009) considered the use of a central regenerator for highly contaminated wastewater treatment as an extension of the work of Li and Chang (2006).

Lee et al. (2013) presented a mathematical technique to integrate batch and continuous processes through the use of storage vessels based on a continuous time approach. Lee et al. (2014) then proposed a four-step mathematical procedure for the minimization of freshwater, storage capacity as well as interconnections between units in a water allocation network (WAN) involving both mass transfer and non-mass transfer based operations.

(c) Hybrid techniques

Oliver et al. (2008) presented a hybrid technique for the synthesis of water reuse network in batch processes. It consisted of a combination of water pinch analysis and mathematical modelling to optimize water utilization in a winery located in Suan

Juan, Argentina. The plant consisted of 30 water using operations with 25 of them being washing operations. Hence, the formulation focused on mass transfer operations. The possibilities for water reuse were first identified using a water pinch technique and the minimum freshwater consumption was obtained. The resultant water network from the pinch analysis required a very large number of storage units to override the time dimension due to the continuous approach employed. A mathematical model was then constructed to provide a cost-effective water reuse network while using the minimum freshwater use obtained from the graphical technique as a lower bound. The model was based on a predefined schedule. However, the mass balance constraints involved in the mathematical model where suitable for semi-continuous processes resulting in a technique that cannot be applied to batch processes.

Foo (2010) developed a MILP formulation for the synthesis of a batch water network with a predefined schedule based on insight concepts of the time-dependent water cascade analysis. Similarly to conventional insight based technique, the technique allowed the minimum freshwater consumption and wastewater generation to be determined prior to the design of the water network. In addition to direct reuse within a time interval and indirect reuse across intervals, regeneration reuse was explored through the use of a wastewater treatment unit. The treatment unit was modelled using a black-box approach with fixed outlet concentration. Both two-step and single step optimisation were used whereby the former was employed to sequentially minimize freshwater use and storage capacity without considering costs. The latter was then used to minimise the total annualized cost of the water network by taking into account the annual freshwater cost, wastewater treatment costs, effluent treatment cost, the capital cost of storage tanks, and the regeneration cost. The cost of regeneration was modelled linearly as a function of the total quantity of water fed into the regenerator. This technique has the advantage including economic aspects such as

cost in the water targeting procedure as opposed to conventional insight based techniques.

2.4.2 Variable schedule techniques

Existing wastewater minimisation techniques that consider a flexible schedule are based on mathematical optimisation due to their complexity. There are no insight-based techniques that have yet been developed to account for scheduling while targeting minimum freshwater use in batch processes. However, a recent effort was made towards the development of a hybrid optimisation technique integrating graphical targeting and mathematical optimisation in wastewater minimisation problems. The aim of the hybridisation is to reduce the complexity of variable scheduling techniques for wastewater minimisation and ease their solution procedures. This section gives a review of existing mathematical and hybrid techniques for the minimisation of wastewater in batch processes with the consideration of a variable schedule.

(a) Mathematical models

Methodologies for freshwater minimisation in batch processes relying on flexible scheduling frameworks arose in the recent decades. The work of Majozi (2005b) was first to consider the simultaneous optimisation of the scheduling and water use in batch processes with a single contaminant. This work was then extended to include both direct and indirect reuse/recycle as wastewater minimisation techniques. Four scenarios were explored in the extended formulation, i.e. fixed outlet concentration and fixed water requirement with and without the presence of water reusable storage. Although the formulation was applied to batch processes with fixed schedules, the formulation was opened to flexibility in scheduling as to increase water reuse opportunities.

Cheng and Chang (2007) then presented an effective procedure for the optimal design of a fully integrated water network where batch schedule, water reuse, and wastewater treatment subsystems were optimised simultaneously. The formulation was aimed at determining the optimum production schedule, the optimum number, and size of buffer tanks and the configuration of the pipeline network. The production schedule was modelled using the STN recipe presentation and the discrete time representation. By sequentially integrating different subsystems, the formulation showed the benefits of simultaneously optimising an integrated schedule and water network through various case studies. The water treatment network consisted of regenerators with either continuous or batch operation mode modelled using a black-box approach with fixed removal ratio, pollutant index, and flowrate limits. The regenerated water was directly disposed to environmental water sinks without exploring any opportunity for reuse within the plant.

Zhou et al. (2009) presented a two-stage model for the sequential optimisation of batch schedule and water network system embedding a regeneration process. The authors attempted to improve on the work presented by Cheng and Chang (2007) by using continuous time approach to address the limitations of discrete time approach. The regenerator was intended to treat highly contaminated wastewater to facilitate its reuse within the process and meet environmental standards for wastewater disposal. The treatment unit was modelled as a black-box where a contaminant removal ratio was used to determine the outlet concentration of the purified water and the percentage of water loss during regeneration was fixed.

Majozi and Gouws (2009) developed a continuous time formulation that simultaneously optimised batch schedule and multi-contaminant water network. Direct and indirect reuse were used as wastewater minimisation techniques but regeneration reuse was not addressed. Li et al. (2010) proposed a mathematical technique to integrate the scheduling framework and WAN of batch processes using a state-time-space (STS) superstructure. A combination of both discrete and continuous

time formulations was used to represent batch schedule based the work of Ierapetritou and Floudas (1998). Chen et al. (2011) presented an RTN based technique targeting maximum plant profit by simultaneously optimising the production schedule and WAN. The formulation considered multiple freshwater sources while exploring direct and indirect reuse of water between units.

Adekola and Majozi (2011) later extended the formulation of Majozi and Gouws (2009) by developing a mathematical modelling technique that considered simultaneous optimisation of batch schedule and multi-contaminant water network that included central water storage and central regeneration unit. However, the regeneration unit was modelled as a black box with a predefined removal ratio for each contaminant and the cost of regeneration was not accounted for in the objective function.

Chaturvedi and Bandyopadhyay (2014a) presented a two-step procedure to optimise a water network with multiple freshwater resources using a flexible scheduling platform. The scheduling model was first solved to obtain the maximum throughput. Next, the water network was optimised while maintaining the throughput at its maximum value. The authors then proposed a dual-objective MILP to optimise a batch water network using a flexible scheduling platform. The first objective function aimed to maximise the production while the second objective consisted of minimising freshwater requirement. The formulation made use of Pareto optimal front to capture the tradeoff between the two objective functions (Chaturvedi & Bandyopadhyay, 2014b).

Adekola and Majozi (2017) recently explored wastewater minimisation in batch plants by adequately selecting the sequence of tasks occurring in a multipurpose unit. Their technique was based on the concept of sequence-dependent changeover operations in which the amount of water required to wash a particular unit after processing a task depends on the succeeding task.

(b) Hybrids techniques

Chaturvedi et al. (2016) recently proposed a hybrid technique using both insight based concepts and mathematical modelling to synthesize a cost-effective batch water network with multiple freshwater resources. Scheduling in their context was made flexible by allowing water sources and demand to be shifted while maintaining production requirements. The formulation claimed that the change in the overall operating cost of a water network does not depend on the number of the available freshwater resources. This was proved by integrating the algebraic algorithm proposed by Chatuverdi and Bandyopadhyay (2012) and mathematical formulations of Chaturvedi and Bandyopadhyay (2014a; 2014b). Therefore the schedule obtained for a batch water network with a single freshwater source was fixed when the problem was extended to multiple resources, thus reducing the model size and computational intensity.

2.5 Consideration of regeneration

The concept of regeneration reuse in batch processes has been considered in the published literature. The work of Liu et al. (2009), Zhou et al. (2009) and Adekola and Majozi (2011) have all explored regeneration reuse as part of the wastewater minimization as discussed in the previous section. However, a black-box approach was used to model the performance of the regenerator in the aforementioned techniques. The main drawback of black-box approaches is their inability to optimize for the energy consumption of regeneration units. The regeneration of wastewater involves the use of wastewater treatment technologies. The type of technology employed strongly depends on the quality of effluents generated and the nature of contaminants to be removed. Membrane systems evolved as effective ways of purifying wastewater and are currently found in many wastewater treatment facilities (Atasi, 2015). However, these technologies require an intensive amount of energy to considerably reduce the contaminant level in wastewater effluents. This highlights

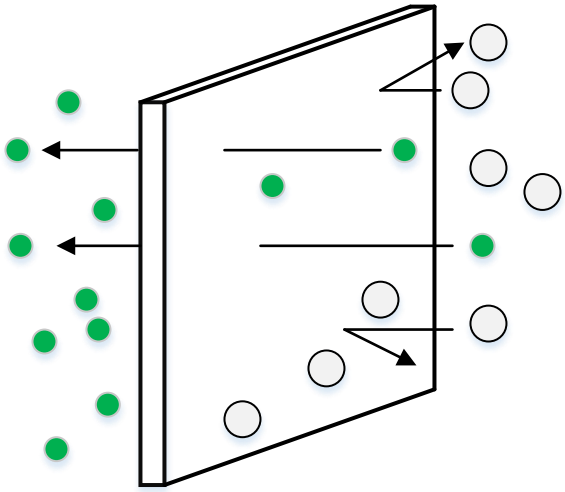
the importance of optimising the consumption of energy in membrane systems while exploring regeneration reuse. This section will give an overview of different membrane technologies used in wastewater reuse and elaborate further on the electrodialysis process, the technology of focus in this work.

2.5.1 Membrane technologies for wastewater treatment

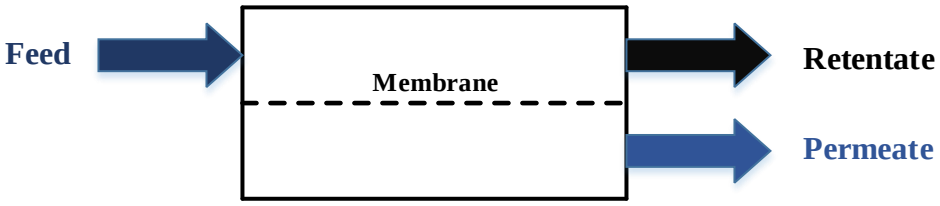
Membrane systems are technologies developed for the removal of species in the aqueous phase by physical or physicochemical mechanisms using a membrane material (Judd & Jefferson, 2003). A membrane material is a thin film which separates two phases by selectively allowing the transport of matters as shown in Figure 2.20(a). The principle of a membrane operation is illustrated in Figure 2.20(b). A feed stream entering a membrane separation is divided into a permeate, the stream containing the materials which have passed through the membrane, and the retentate, which is made of all the non-permeable materials (Mallevialle, et al., 1996).

Membrane processes are becoming popular for bulk water and wastewater treatment due to the following advantages that they offer over conventional water treatment techniques (Judd & Jefferson, 2003).

- Less energy consumption due to the inexistence of a phase change.
- The build-up on membrane surfaces are minimal. This can guarantee a smooth continuous operation of the treatment process
- Little or no addition of chemicals is usually required during separation.
- High selectivity
- Production of high quality treated effluents



(a)



(b)

Figure 2.20 *Principle of a membrane operation*

There is a wide range of membrane operations that can be used for the treatment of industrial wastewater. They can be classified based on the driving force, the mechanism of separation, the structure of the membrane and the phases in contact as presented in Table 2.1. The driving force is the criteria commonly used to characterize membrane operations. In this regards, Pressure, activity and electrical potential driven operations are the three main types of membrane operations. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are all operations in which the pressure difference across the membrane drives the separation process in which the solvent is transferred through the membranes. On

the other, Pervaporation (PV), membrane distillation (MD), membrane stripping (MS) operate based on the activity difference across the membrane which causes the membrane to selectively allow the transport of the solvent. Dialysis (DIA) is also an activity driven membrane in which, unlike the other three aforementioned activity driven membrane, the concentration difference allows the transport of solutes through the membrane. Electrodialysis (ED) is membrane operation in which the potential difference causes ions to selectively pass through the membranes.

Table 2.1 *Classification of membrane operations (Mallevialle, et al., 1996)*

Membrane operation	**Driving force**	**Mechanism of separation**	**Membrane structure**	**Phase**	
				1	**2**
Microfiltration	Pressure	Sieve	Macroscopic	L	L
Ultrafiltration	Pressure	Sieve	Mesopores	L	L
Nanofiltration	Pressure	Sieve+(solution/diffusion+eclusion)	Micropores	L	L
Reverse osmosis	Pressure	Solution/diffusion+exclusion	Dense	L	L
Pervaporation	Activity (Partial pressure)	Solution-diffusion	Dense	L	G
Membrane stripping	Activity (Partial pressure)	Evaporation	Macropores (gaz membrane)	L	G
Membrane distillation	Activity (temperature)	Evaporation	Macropores (gaz membrane)	L	L
Dialysis	Activity (concentration)	Diffusion	Mesopores	L	L
Electrodialysis	Electrical potential	Ion exchange	Ion exchange	L	L

The membrane structure and the mechanism of separation are key indicators of the type of contaminant a membrane operation can remove during the treatment of wastewater. MF and UF are both suitable for the removal of solid particles from water through sieving. The difference in membrane pore size makes UF capable of removing smaller particles as compared to MF. NF, on the other hand, is mainly suitable for the removal of multivalent ions such as calcium and magnesium. RO has

a dense membrane structure which is tailored to retain salts and low molecular weight solutes. PV and MS can be used for the removal of volatile organic compounds. MD can also be applied for the removal of salts in wastewater. DIA selectively allows ions and low molecular weight solutes to pass through the membrane while rejecting larger colloidal and high molecular weight solutes. ED is mainly designed for the removal of ionic species such as salts, acids, and nitrate from wastewater.

This research focused on implementing an ED treatment unit to facilitate the purification of wastewater generated from batch water network. The main purpose this implementation is to demonstrate the benefits of embedding a design model of a wastewater treatment unit while synthesizing a batch water network. It is worth mentioning that any other membrane operation can be used in this work depending on the type of contaminants found in wastewater generated from a given plant. A detailed analysis of the operation and design of the ED system is given in this section.

2.5.2 Electrodialysis technology

(a) Basic concepts

Electrodialysis (ED) is a membrane separation process which is based on the electro-migration of ions through perm-selective membranes (Tsiakis & Papageorgiou, 2005). In the ED stack, a series of cation- and anion-exchange membranes are alternatively arranged between a cathode and anode to form dilute and concentrated cells. The applied direct current (DC) establishes an electric field between the cathode and the anode. When an ionic solution is pumped through the cells, the electric field causes the migration of cations and anions towards the cathode and anode respectively, The positively charged ions pass through the negatively charged cation-exchange membranes (CEMs) but are retained by the anion-exchange membranes (AEMs). Likewise, the anions pass through the positively charged AEMs and are retained by the CEMs. Therefore, there is an increase of ions in one compartment and ion depletion in the other. This results in the formation of the diluate (depleted

solution), and the brine (concentrated solution). An ED stack consists of a series of cell pairs, and a single cell pair contains a CEM, AEM, a diluate and a concentrate compartment (Rohman & Aziz, 2011; Strathmann, 2004). The schematic representation of the ED stack is shown in Figure 2.21. Depending on the degree of desalination required in a plant, multiple ED stacks can be placed in series in order to achieve a higher contaminant removal.

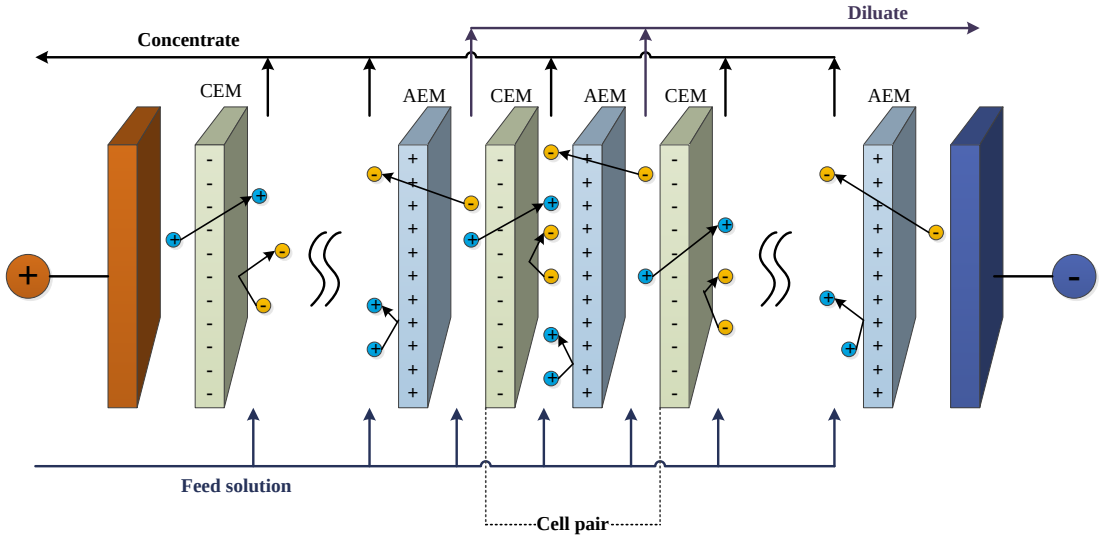


Figure 2.21 *Schematic diagram illustrating the principle of ED desalination stack containing CEMs and AEMs in alternating series (Strathmann, 2004).*

(b) Advantages and limitations of Electrodialysis

There are quite well-established technologies for the selective removal of salts from aqueous solutions. These technologies are generally used in industrial applications where salts are final products or limit further purification of the final products. However, these technologies are of little use in low-value applications such as wastewater treatment (Silva, et al., 2013). Membrane processes competing directly with ED in water desalination applications are reverse osmosis (RO) and recently nanofiltration (NF). ED has proven to be advantageous over RO and NF in applications with medium plant capacity of 100 to 20 000 cubic meters per day with

wastewater or brackish water salinity ranging from 100 to 5000 milligrams per liter of total dissolved solids. However, RO has proven to be economically viable in large-scale plants with higher salts concentration. This is due to the fact that, in ED, energy consumption and the required membrane area are directly proportional to the salt concentration of the water fed to the process. Nevertheless, ED has also been used for the treatment of well water of a total salt concentration of about 36 000 milligrams per liter (Strathmann, 2004).

The advantages of ED over RO, NF and other pressure-driven membrane processes include, among others, self-cleaning of membranes over a long-term operation, tolerance of elevated temperature, less raw material pretreatment and easy start-up and shut-down procedure for processes with intermittent operations (Strathmann, 2004; Silva, et al., 2013). Therefore ED has gained more interest in various applications such as brackish water desalination (Ortiz, et al., 2005), treatment of RO concentrate (Zhang, et al., 2012), wastewater minimization (Silva, et al., 2013).

(c) Design and optimisation of an electrodialysis process

The design of an ED unit takes into account the actual ED stack, power supply and several other components such as pumps, process control devices and feed solution pretreatment equipment. Different operation modes can be adopted in the design of ED process. This includes batch mode, continuous mode, and feed-and-bleed mode with partial recycling of diluate and concentrate streams. The choice of ED operation mode depends on the degree of desalination required and the feed stream composition (Mintz & Shaffer, 1980; Strathmann, 2004).

The design and optimization of ED process have been on the research agenda for years. Korngold (1982) conducted an experimental optimization of an industrial ED unit to determine the effect of some of the several basic design parameters on the energy requirement. Lee et al. (2002) then presented a mathematical model for the

design and optimization of an electrodialysis process for brackish water desalination in order to evaluate its performance at the design level. The authors gave a detailed derivation of design equations and experimental methods for the determination of design parameters. The objective of the formulation was to minimize total costs of the desalination process which was the sum of capital and operating costs. An iterative procedure was adopted in the solution procedure of the design model. Tsiakis and Papageorgiou (2005), improved on earlier work by presenting a MINLP model for the design and optimization of ED process. A multistage feed and bleed model for ED operation was introduced and an adequate solution approach was adopted.

2.6 Solution approaches to wastewater minimisation problems

Optimisation approaches for wastewater minimisation in batch plants involve either graphical, algebraic or mathematical modelling concepts. Graphical and algebraic techniques are readily solved by the modeller using graphs and algebraic algorithms as discussed in the previous sections. Mathematical models for wastewater minimization, on the other hand, are usually MINLP problems which are solved using complex algorithms. Some optimisation solvers for mathematical programming are built in commercial optimization packages to ease the solution process. This section thus discusses the issue of convexity in mathematical programming, which is a concept on which solution algorithms are based. The various solutions techniques and existing optimization solvers for MINLP models are also presented.

2.6.1 Convexity in mathematical programming

Nonlinear programming models are divided into convex and non-convex models. Convexity in mathematical programming allows the modeller to predict whether a single optimum value exists or global and multiple other local optimum values are found in the search space of a specific problem (Edgar & Himmelblau, 1988). A

convex programming model involves a convex objective function to be minimized or maximized over a convex region. A convex region is defined as an optimization search space where a straight segment joining two points in the region lies within that region. The opposite holds for non-convex regions as shown in Figure 2.22.

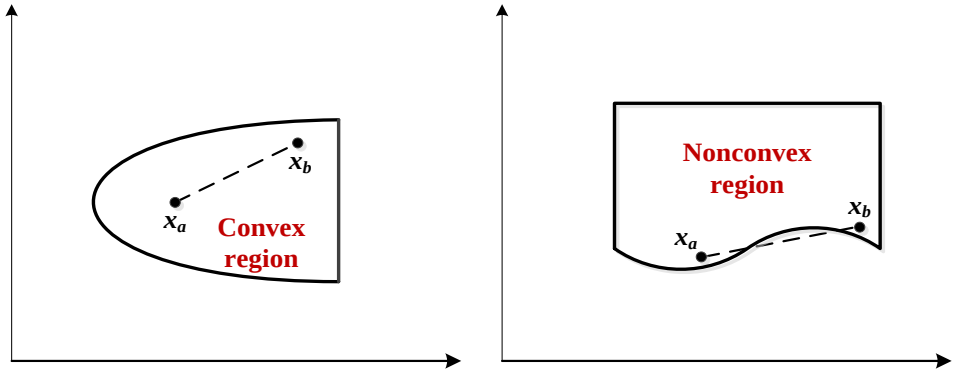
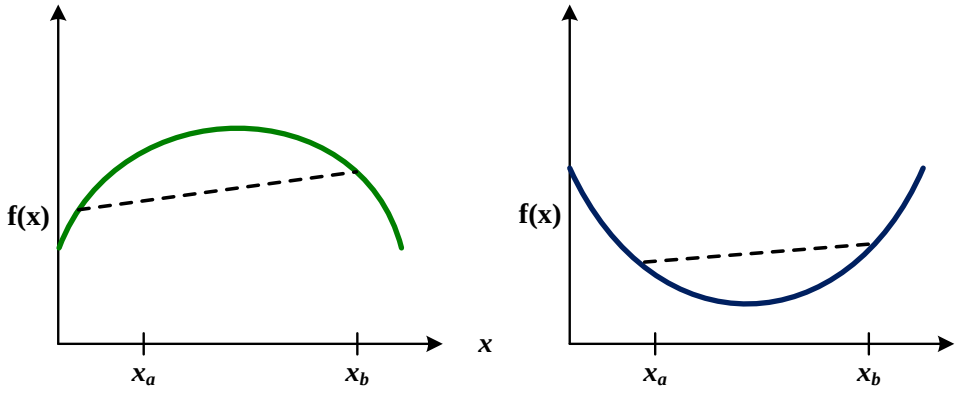


Figure 2.22 *Convex and Non-convex regions (Edgar & Himmelblau, 1988)*

A function is said to be convex when all the infinite set of points satisfying the function forms a convex *region* (Williams, 2013). A condition for any function, *f*, to be called convex over a region *R* is presented by constraint (2.17).

$$-f[\theta x_a + (1-\theta)x_b \leq \theta f(x_a) + (1-\theta) f(x_b) \qquad (2.17)$$
$$\forall x_a, x_b \in R$$

Where θ is a scalar that can take any value between 0 and 1 and x_a and x_b are any two distinct values of *x*. It is worth pointing out that the condition for *f* to be classified as a concave function is similar to constraint (2.12). The only differences are the omission of the negative sign and replace the replacement of the "greater or equal to" ($\leq$) symbol by the "less or equal to" ($\geq$) symbol in the above inequality (Edgar & Himmelblau, 1988). This implies that convex function has a single minimum point while a concave function has a maximum point as shown in Figure 2.23.



(a) Concave function **(b) Convex function**

Figure 2.23 *Comparison between (a) Concave and (b) Convex functions (Edgar & Himmelblau, 1988)*

A nonconvex function, on the other hand, exhibits a different behavior as graphically represented in Figure 2.24. It shows the existence of multiples optimum points among which are global optimum points such as points *d* and *e*. For this reason, nonconvex problems are difficult to solve compared to convex programming problems. Therefore, complex algorithms are required to guarantee a globally optimal solution to a nonconvex problem (Williams, 2013).

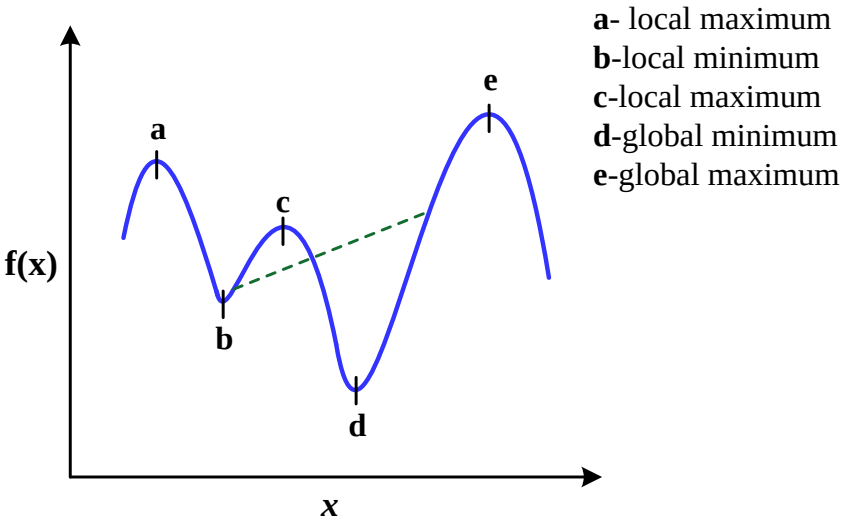


Figure 2.24 *A graphical representation of a nonconvex function (Edgar & Himmelblau, 1988)*

2.6.2 Convexification techniques

MINLP solutions algorithms discussed in the previous section were initially developed for convex problems. Although the algorithms can be applied to non-convex models, difficulties could arise when solving MILP master problems and NLP subproblems. MILP master solutions may not provide valid lower bound while NLP subproblems suffer the possibility of having multiples local optimum values (Grossmann, 2002). There exist many ways of circumventing these problems and among them include linearization and reformulations techniques. These methods are broadly referred to as convexification techniques and will be briefly discussed in this section.

(a) Glover transformation

Glover transformation (Glover, 1975) is an exact linearization technique which eliminates nonlinear terms by replacing them with a set of linear constraints. This technique deals with a case where polynomial functions contain bilinear terms *xy* in

which a continuous variable x is multiplied with a binary variable y. The transformation is performed as follows:

A new continuous variable r is introduced such that

$$r \underset{replace}{=} xy \tag{2.18}$$

It is assumed that lower and upper bounds of variable x are given as shown in constraint (2.19). Additional constraints ensuring that z takes the appropriate values are then constructed as shown by constraints (2.20) and (2.21).

$$x^U \geq x \geq x^L \tag{2.19}$$

$$x^L y \leq r \leq x^U y \tag{2.20}$$

$$x - x^U(1-y) \leq r \leq x + x^L(1-y) \tag{2.21}$$

Constraint (2.20) is obtained by multiplying constraint (2.19) by y to apply bounding conditions of variable x to variable r. On the other hand, constraint (2.21) equates r to x when the binary variable y takes a value of 1. Therefore, the Glover transformation of the bilinear term xy is given by constraints (2.19)- (2.21).

(b) McCormick over- and under-estimators

McCormick (1976) proposed a methodology to obtain global solutions of nonconvex nonlinear programming problems. It involves the generation of convex and concave envelopes for factorable functions with bilinear terms. This can be applied to solution algorithms of nonconvex MINLPs to provide tight convex relaxations, hence decreasing computational difficulties. The procedure for obtaining convex underestimators and concave overestimators of bilinear terms can be summarized as follows.

Given a polynomial consisting of bilinear terms *xy* in which *x* and *y* are continuous variables, a new continuous variable *m* is introduced to replace *xy* in the function as shown in constraint (2.22) below.

$$m = xy \tag{2.22}$$

Variables *x* and *y* are each provided with lower and upper bounds and this is shown in constraints (2.23) and (2.24)

$$x^U \geq x \geq x^L \tag{2.23}$$

$$y^U \geq y \geq y^L \tag{2.24}$$

Constraints (2.23) and (2.24) are then decomposed and rearranged to form constraints (2.25)-(2.28) below.

$$x^U - x \geq 0 \tag{2.25}$$

$$x - x^L \geq 0 \tag{2.26}$$

$$y^U - y \geq 0 \tag{2.27}$$

$$y - y^L \geq 0 \tag{2.28}$$

By multiplying Constraint (2.25) with (2.27) and replacing *xy* by *m*, the following constraint is obtained.

$$m \geq xy^U + x^U y - x^U y^U \tag{2.29}$$

Similarly, multiplications of the set of constraints ((2.26);(2.28)), ((2.25);(2.28)) and ((2.26);(2.27)) lead to Constraints (2.30)-(2.32) below.

$$m \geq xy^L + x^L y - x^L y^L \tag{2.30}$$

$$m \geq xy^L + x^U y - x^U y^L \tag{2.31}$$

$$m \geq xy^U + x^L y - x^L y^U \tag{2.32}$$

Therefore, the underestimators of function *xy* are represented by constraints (2.29) and (2.30) while the overestimators are given by Constraints (2.31) and (2.32). This is graphically illustrated by Figure 2.25.

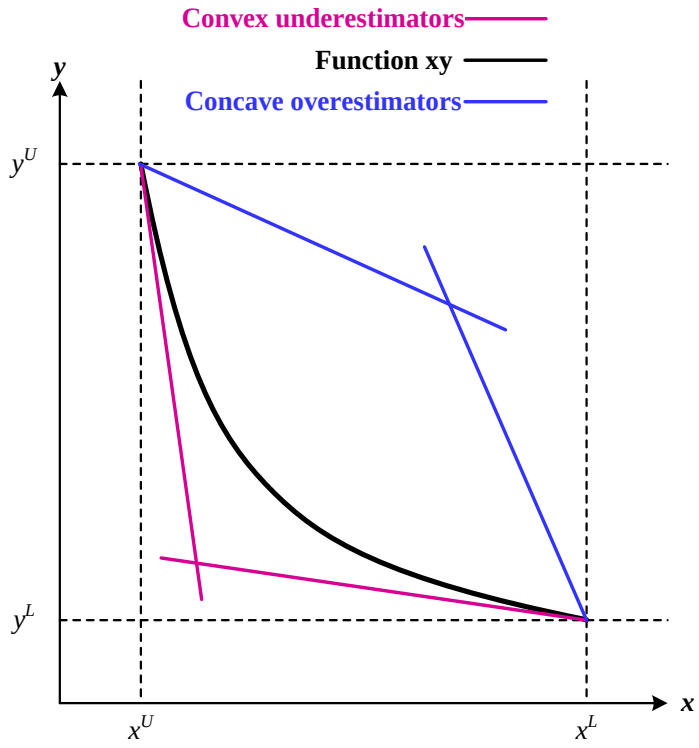


Figure 2.25 *Graphical representation of McCormick (1976) envelopes*

(c) Reformulation framework of Lundell et al. (2013)

Lundell et al. (2013) formulated a global optimization framework that implements α-BB underestimators in the signomial global optimization (SGO) algorithm. They aimed to provide a general algorithm for all twice differentiable functions of nonconvex MINLP problems. The SGO technique was developed throughout the years starting from the work of Porn et al. (1999) to the contribution of Lundell and Westerlund (2012). It employs single-variable exponential or power transformations to convexify nonconvex signomial functions. A signomial function is a mathematical expression made up of signomial terms, i.e. products of power functions. An explicit mathematical expression of a signomial function of *N* variables and *J* signomial terms is as follows:

$$\sigma(x) = \sum_{j=1}^{J} c_j \prod_{i=1}^{N} x_i^{pji} \tag{2.33}$$

Where *cj* and *pji* are real-valued parameters. Special types of signomial functions commonly found in mathematical programming models are polynomial functions with bilinear and trilinear terms. Piecewise Linear Functions (PLFs) are used in the SGO algorithm to capture the relationship between transformation and original variables which then provide an overestimation of the nonconvex feasible region. A global solution is found by iteratively updating the PFLs, i.e. iteratively adding breakpoints to the PLFs, until the solution to the overestimated problem converges.

The α-BB method, on the other hand, is used to obtain convex underestimator of nonconvex functions. It was first introduced by Liu and Floudas (1993) and Maranas and Floudas (1995). The underestimation is achieved by adding a quadratic function to the original nonconvex function in order to suppress any nonconvexity as shown in Constraint (2.34).

$$g(x)+\sum_{i=1}^{N}\alpha_i(x_i-\underline{x}_i)(x_i-\bar{x}_i)\le g(x)\ ,\ \forall x_i\in[\underline{x}_i,\bar{x}_i] \tag{2.34}$$

The value of parameter α in Constraint (2.34) determines the tightness of the α-BB underestimator and the ideal case is to choose the smallest α value. Figure 2.26 gives an illustration of the convex underestimation of a one-dimensional sinusoidal function where the x-domain is partitioned into two intervals. The underestimation is carried out at each interval and α-values are specified for each interval. In general, the tightest α-value for the underestimation of a unidimensional function, i.e. *i=1*, can be found by taking the second derivative of the left-hand side of Constraint (2.34) and satisfying the condition given by Constraint (2.35). However, α values for multi-dimensional functions are obtained using different techniques as proposed by Adjiman et al. (1997).

$$\alpha\ge-\frac{1}{2}g''(x),\ \forall x\in[\underline{x},\bar{x}] \tag{2.35}$$

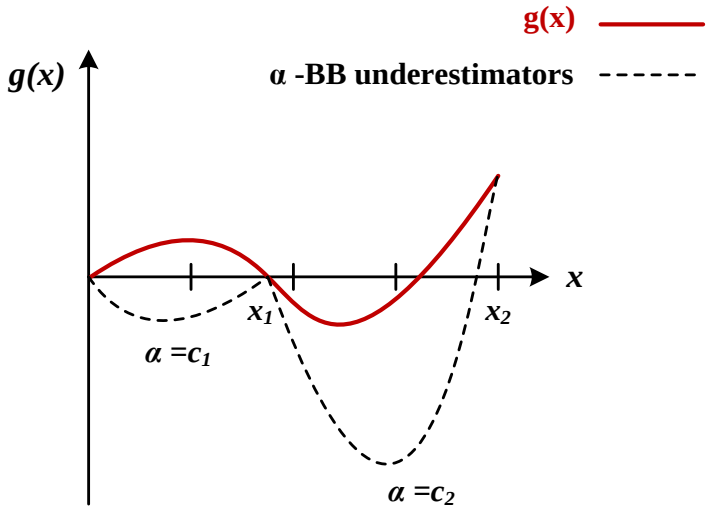


Figure 2.26 *α-BB underestimation of a typical nonconvex function g(x) (Lundell, et al., 2013)*

The implementation of α-BB underestimator in a Branch and Bound framework usually yields a piecewise convex domain similar to the one shown in Figure 2.26. This is due to the fact that different α values are used at different nodes of the search tree where each node correspond a variable interval (Lundell, et al., 2013). The method of Lundell et al. (2013) extended the convexity to the entire variable-space by implementing the α-BB underestimator in a piecewise linear reformulation of the SGO algorithm. The α-BB underestimator was modified by neglecting the lower and upper bound of variable *x* to allow the convexification of the entire *x*-space provided that the value of parameter α is large enough as shown in Constraint (2.36).

$$g(x)+\alpha x^2-\widehat{W}\le g(x)+\alpha x^2-W=g(x) \tag{2.36}$$

$$W\ge \alpha x^2 \tag{2.37}$$

The term $g(x)+\alpha x^2-\widehat{W}$ in Constraint (2.36) is the reformulated convex underestimator of nonconvex function $g(x)$ where $\widehat{W}$ is the tightest linear overestimation of the compensation factor *W*. It is obtained by performing piecewise linearization of function $W=ax^2$ with breakpoints $(x,\alpha x^2)$ as shown in Figure 2.27. A general condition for the underestimation of a one-dimensional function to be obtained is given by Constraint (2.37).

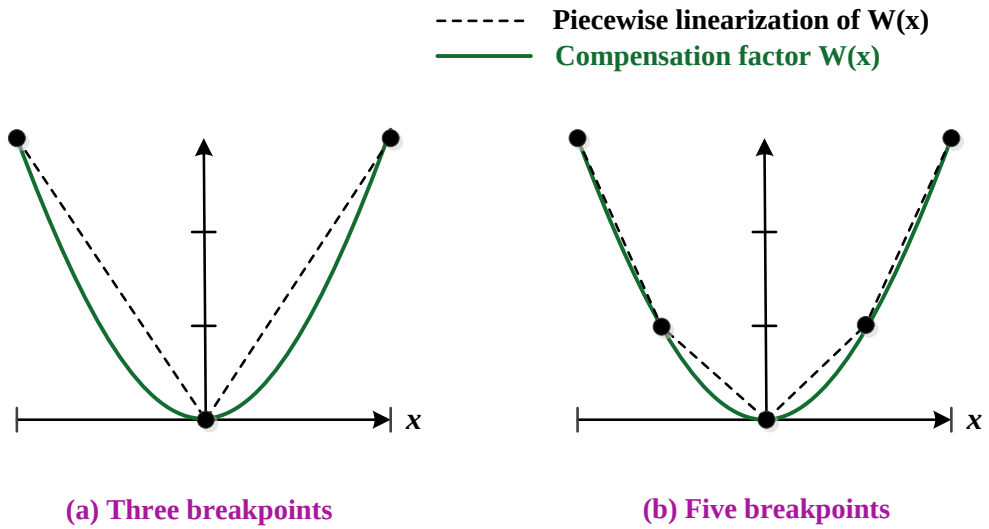


Figure 2.27 *Compensation function W(x) and its overestimation $\hat{W}(x)$ obtained by PLFs with (a) three and (b) five breakpoints (Lundell, et al., 2013)*

For a multidimensional function of N variables, the convex underestimator is obtained by replacing the nonconvex constraint (2.38) with the generalized convex underestimator given by constraint (2.39).

$$g(x) \le 0, \quad x = (x_1, x_2, x_3, ..., x_N) \tag{2.38}$$

$$g(x) + \sum_{i=1}^{N} \alpha_i x_i^2 - \widehat{W} \le 0 \tag{2.39}$$

In the general formulation, the compensation factor W is obtained using Constraint (2.40) below. It is worth mentioning that the implementation of α-BB underestimators in the SGO algorithm does not suppress the use of power and exponential transformations as they can provide tighter underestimation of signomial functions in many cases.

$$W = \sum_{i=1}^{N} \alpha_i x_i^2 \tag{2.40}$$

2.6.3 Solution algorithms for MINLP problems

MINLP models are commonly encountered during the optimization of various chemical and industrial processes. As previously mentioned, an MINLP model entails the existence of both continuous and integer variables as well as the presence of nonlinear terms in the existing constraints and/or objective function. MINLP problems are computationally difficult to handle, hence they fall under the class of NP-complete problems (Kallrath, 2000). This is mainly due to the fact they inherit from the combination of variables found in MIP models and nonlinearity and convexity issues associated with NLP models (Bussieck & Pruessner, 2003).The general algebraic form of and MINLP problem is as follows:

$$min \qquad Z = f(x,y) \tag{2.41}$$

$$s.t \qquad g_j(x,y) \leq 0 \tag{2.42}$$

$$\forall j \in J, x \in X, y \in Y \tag{2.43}$$

Where *f(.), g(.)* are differentiable functions, *J* is the index set of inequality constraints, and *X* and *Y* are sets of continuous and discrete variables respectively (Grossmann, 2002).

Solving MINLP models has been the subject of many research studies and different algorithms have been developed to provide optimal solutions to MINLP problems. Effective deterministic approaches to these types of models include the *Branch and Bound (BB), Generalized Benders Decomposition* (*GBD), Outer Approximation (OA) and extended cutting plane (ECP)* algorithms.

(a) Branch and Bound (BB)

The BB method was first introduced by Dakin (1965) to provide solutions for MILP problems. It was later adapted by Gupta and Ravindran (1985) to consider MINLP problems. The BB algorithm starts by solving the relaxed MINLP model where all integer variables are relaxed thus allowing them to take both integer and fractional values within existing boundaries. This relaxation transforms the original MINLP problem into an NLP subproblem. If the subproblem yields a solution where all integer variables have discrete values, the search is stopped and the solution is regarded as optimal. Otherwise, a tree search is performed in the space of integer variables. The tree is constructed by successively fixing integer variables at corresponding nodes and solving an NLP subproblem at each node. The NLP subproblem at the kth node of the tree search for the problem described by Constraints (2.41)-(2.43) takes the following format:

$$min \quad Z_{LB}^{k} = f(x,y) \tag{2.44}$$

$$s.t \quad g_j(x,y) \le 0, \quad \forall j \in J, x \in X, y \in Y_R \tag{2.45}$$

$$y_i \le \alpha_i^k, \qquad \forall i \in I_{FL}^k \tag{2.46}$$

$$y_i \le \beta_i^k, \qquad \forall i \in I_{FU}^k \tag{2.47}$$

where Y_R is the continuous relaxation of set Y, I_{FL}^k and I_{FU}^k are subsets of indices $i \in I$ for integer variables y_i that are restricted to lower bound α_i^k and upper bound β_i^k. The solution to the subproblem in one node provides a lower bound for subproblems in descendant nodes and so on. A feasible integer solution, on the other hand, sets an upper bound for the descendant nodes. Fathoming of nodes is performed in instances where a lower bound exceeds the current upper bound, an infeasible solution is obtained, or all integer variables take discrete values (Grossmann, 2002). Fathoming is defined as the process of discarding or deleting a current subproblem and all of its descendants (Borchers, 1992). Once the search is completed, the best option among the feasible solutions found at certain nodes is regarded as the optimal solution.

(b) Generalized Benders Decomposition (GBD)

The GBD algorithm (Geoffrion, 1972) starts by categorizing variables into complicating and non-complicating variables. In the case of MINLP models, discrete variables fall under the complicating category since their presence makes the model harder to solve. A common example of integer variables is a binary variable which can either take a value of 0 or 1. The problem is then decomposed into MILP master problems and NLP subproblems and solved sequentially in the space of complicating variables. The solution to the NLP subproblem provides an upper bound for the original MINLP while the MILP master problem yields a new set of discrete variables for the subsequent NLP subproblem. NLP subproblems are generated by fixing complicating variables to a given value while the master problem is obtained by deriving a Lagrangian function parameterized in discrete variables at each subproblem. In convex optimization, the master problem provides a lower bound. Convergence occurs when the lower and upper bounds have the same value or are within the desired tolerance. The solution is then regarded as the optimal solution for the MINLP problem. A flowchart of the GBD algorithm is given by Figure 2.28.

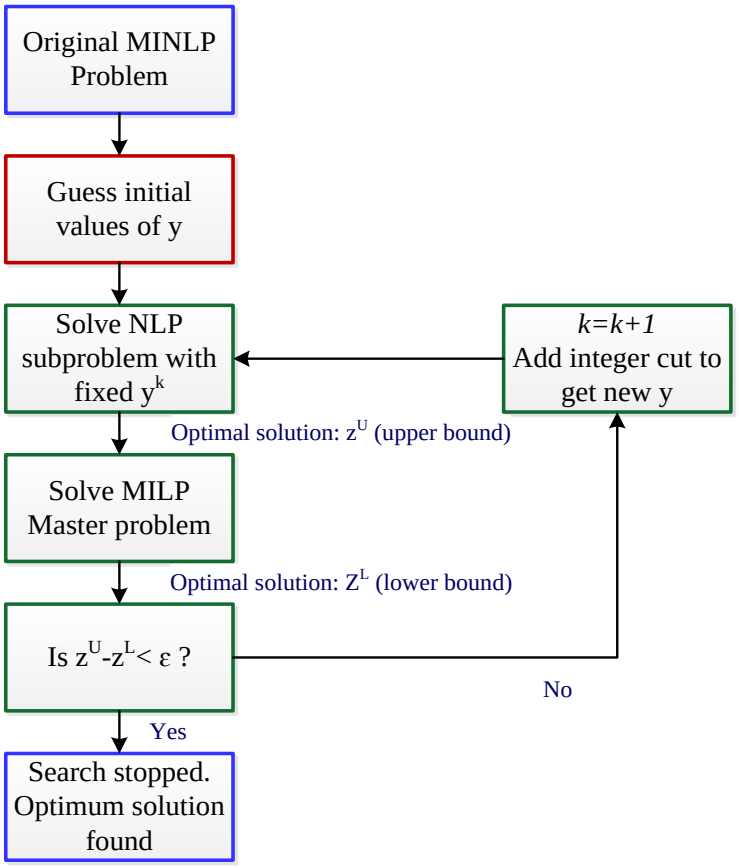


Figure 2.28 *GBD and OA solution procedure for MINLP models*

(c) Outer Approximation (OA)

The OA algorithm, developed by Duran and Grossman (1986) is similar to the GBD method hence follows the same flowchart depicted by Figure 2.28. The difference resides in the definition of the MILP master problem. In this case, the master problem is obtained by performing an outer approximation, i.e. linearization or Taylor series expansions, of the nonlinear constraints at optimal points of NLP subproblems (Kallrath, 2000). This is graphically illustrated in Figure 2.29. For this reason, the OA algorithm provides tighter bounds and requires fewer iterations for the problem to converge when compared to the GBD algorithm.

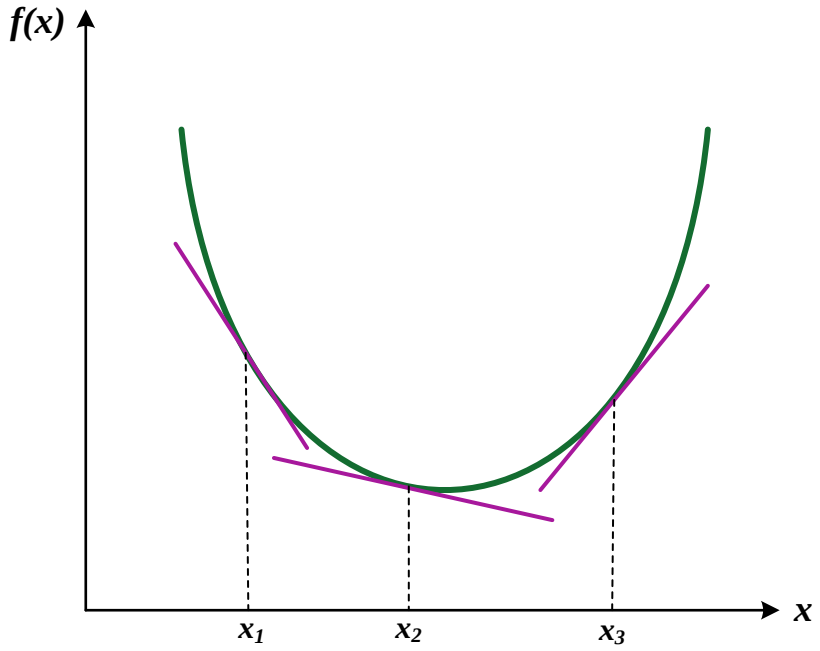


Figure 2.29 *Outer approximation (at three points) of a convex function in R^1 (Duran & Grossmann, 1986)*

(d) Extended cutting plane (ECP)

The ECP method for solving MINLP model was presented by Westerlund and Pettersson (1995). It is an extension of the cutting plane algorithm of Kelley (1960) developed to provide solutions for Convex NLP. This method omits the use of NLP subproblems and relies only on an iterative procedure of the MILP master problems. The master problem in ECP is defined identically to the OA master problem. The iteration is performed by successively adding the most violated constraint at predicted points and convergence is achieved when the maximum number of violated constraints lies within the tolerance. This method has the disadvantage of requiring a large number of iterations since discrete and continuous variables are simultaneously converged (Grossmann, 2002). Consequently, the ECP is best suited to provide solutions for MINLPs of moderate size.

2.6.4 Available optimization solvers for MINLP models

Various commercialized and open source solvers which can readily handle MINLP problems are available to end-users and programmers. These algorithms differ from each other by their built-in features to solve specific types of MINLP models to either local or global optimality. MINLP algorithms often need to be customized for specific MINLP problems amongst their wide range of applications. Moreover, certain solvers for MINLP result from a combination of MIP, LP and NLP solvers. The two aforementioned reasons explain why many commercial and free MINLP solvers are embedded into modelling systems such as GAMS, AMPL, AIMMS, etc. Nevertheless, there also exist many other solvers which can be readily used independently of modelling languages (Bussieck & Vigerske, 2014).

The General Algebraic Modelling System (GAMS) is a well-established and user-friendly modelling language which was introduced in 1970 and has been developed and improved throughout the years. GAMS is designed to model and to solve linear, nonlinear and mixed integer programming problems for complex and large scale optimization problems. It contains both commercial and free solvers for MINLP problems which include BARON, DICOPT, SCIP, LINDO, etc. A Mathematical Programming Language (AMPL) and the Advance Interactive Mulltidimensional Modelling System (AIMMS) are other widely used algebraic languages which both appeared in the late 19's (Fourer, et al., 1993; Bisschop & Roelofs, 1999). The NEOS server is another robust server which gives access to more than fifty academic and commercial optimization packages through internet interfaces. It was first announced in 1995 and resulted from a collaborative and multi-institutional effort to develop computational servers and cooperative technologies. It allows users to send tedious and computational intensive optimization problems generated in either GAMS or AMPL modelling systems and select the desirable solver among the available solvers depending on the nature of the model (Dolan, et al., 2002).

The DICOPT (DIscrete and Continuous OPTimizer) algorithm is amongst the earliest solvers capable of solving MINLP problems. It was developed by the research group of I. E. Grossmann at the Engineering Design Center of Carnegie Mellon University and is a commercial solver available within GAMS. The solution algorithm is based on the OA algorithm of Duran and Grossmann (1986) and the Equality-Relaxation (OA/ER) which is an extension of the OA performed by Kocis and Grossmann (1987a) in conjunction with NLP advanced solvers such as MINOS. DICOPT can guarantee global optimal solutions for convex MINLPs by using the OA algorithm whereas, for nonconvex MINLPs, Equality Relaxation (ER) is introduced. It consists of replacing nonlinear equality constraints with sets of inequalities constraints where nonlinear functions are linearized. However, global optimum solutions are not guaranteed for nonconvex MINLPs. The AOA (AIMMS Outer Approximation) can also be named amongst OA based solvers. It is an open source solver integrated into the AIMMS system.

There also exist Branch and Bound based MINLP solvers which use NLP relaxations. Among them include the αBB (α-Branch-and-Bound) which was developed by the research group of C. Floudas at the Computer-Aided Systems Laboratory of Princeton University (Androulakis, et al., 1995). It is a global optimization solver for nonconvex problems which is only made available to their research collaborators (Bussieck & Vigerske, 2014). The SBB (Simple Branch-and-Bound) is another branch and bound based commercial solver available within GAMS (GAMS Development Corp., 2014).

Other types of solvers make use of convexification techniques in a branch and cut algorithm to solve both convex and nonconvex models to global optimality. BARON (Branch- And-Reduce-Optimization Navigator) is one of such algorithms. It is a commercial solver that can be accessed within both AIMMS and GAMS. The Solver implements a branch and bound procedure that use LPs for bounding and not NLPs as used in conventional branch and bound technique for MINLP models. The Linear

relaxation of MINLP is obtained through linear outer approximation which entails reformulating the problem by adding auxiliary variables such that it only contains nonconvex terms for which convex underestimators or concave overestimators are known. The branch and bound algorithm is enhanced by using duality techniques to reduce the number of variables during the solution procedure (GAMS Development Corp., 2014). ANTIGONE is another solver of that kind available within GAMS as a commercial solver. Unlike BARON, ANTIGONE uses MIPs for bounding in the branch and bound algorithm (Misener & Floudas, 2014)

2.7 Summary

This chapter gave detailed explanations of the various elements considered in the design and optimization of a batch process. A literature review of the existing techniques developed for the short-term scheduling of batch processes and the minimization of wastewater generated by a batch water network was also performed. It was observed that regeneration reuse, a technique used to minimize the consumption of freshwater in batch processes, had not been thoroughly explored. Moreover, no work that includes a detailed design model of a regeneration unit while simultaneously optimizing batch schedule and water network had yet been performed. This implies that the minimization of the amount of energy consumed by regeneration units while optimizing the freshwater consumption of batch processes has been overlooked. Therefore, the focus of this research study on developing a mathematical formulation aiming to simultaneously minimize the freshwater use and regeneration energy use of multipurpose batch processes while optimizing their production schedule is justified. The next chapter will present and explain the novel mathematical technique proposed for the optimization of multipurpose batch plants.

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3

MODEL DEVELOPMENT

3.1 Introduction

This chapter presents the mathematical model developed in this work to design and synthesize a sustainable and cost-effective multipurpose batch plant. The MINLP formulation is based on the superstructure depicted by Figure 3.1. It shows all possible interconnections between batch processing units represented by *j* and *j'*, the storage tanks and the regenerator. It is worth mentioning *j* and *j'* can represent the same units or different processing units that are directly integrated. Moreover, the number of storage tanks as depicted by the superstructure is not subject to change. This results from the fact that two storage tanks are required in order to connect batch operations to the semi-continuous regeneration process. The proposed formulation is divided into comprehensive sections depicting major components of the model developed. This includes the scheduling model, the set of constraints for the water balance around processing units and storage tanks, the set of constraints pertaining to the design of the ED unit and finally constraints ensuring adequate sequencing of tasks and events within the plant. Each aforementioned section is elaborated in this chapter and the major assumptions made in the formulation are also stated.

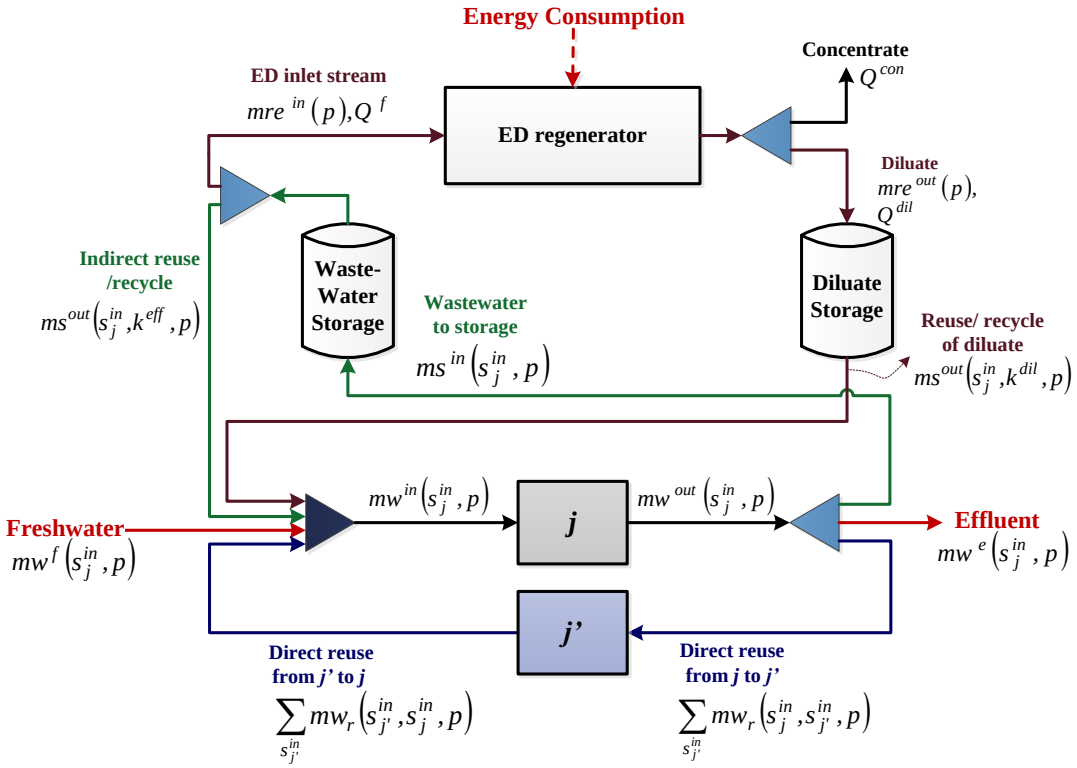


Figure 3.1 *Water network superstructure for the proposed formulation*

3.2 Scheduling model

The scheduling model ensures that the time dimension which is inherent in batch processes is captured. It determines the time at which a specific task happens, the size of the processed batch and the sequencing of tasks within a given time horizon. The scheduling model adopted in this formulation was developed by Seid and Majozi (2012). It is a unit specific slot-based formulation in which, for each unit, a processing task and its subsequent washing operation are modelled to occur within the same time slot *p* with unknown duration as illustrated in Figure 3.2. The model has proven to be robust in terms of handling shared resources and requires fewer time points compared to other formulations. The formulation includes allocation constraints, material balance constraints, duration constraints, sequencing constraints,

storage constraints for processing materials, tightening and time horizon constraints. The details about the scheduling model are given in Appendix A

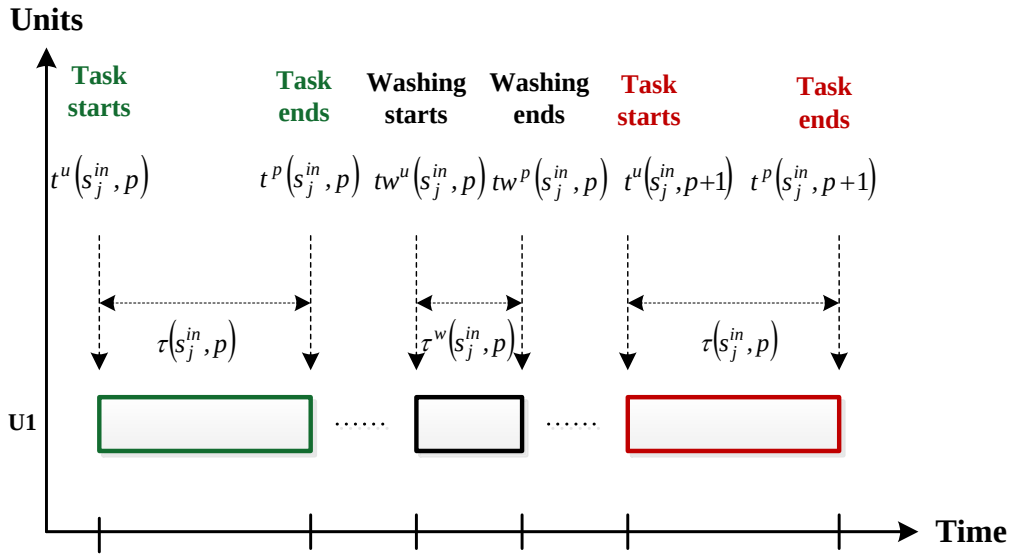


Figure 3.2 *Scheduling model concept for batch processes*

3.3 Material balance for the water network

3.3.1 Water balance constraints for washing operations

The material balance around each water-using operation is given by Constraints (3.1), (3.2), and (3.3) following the superstructure depicted in Figure 3.1. Constraint (3.1) states that the amount of water entering any processing unit at any time slot *p* is made up of freshwater and/or the amount of water received from other units and storage tanks. Constraint (3.2) states that the amount of water leaving a unit can be directly reused to other processing units, sent to storage for later reuse and/or directly disposed as an effluent. Constraint (3.3) ensures that the amount of water entering and leaving an operation is conserved at any given slot *p* assuming no water loss in the system.

$$mw^{in}\left(s_j^{in},p\right)=mw^{f}\left(s_j^{in},p\right)+\sum_{s_{j'}^{in}}mw^{r}\left(s_{j'}^{in},s_j^{in},p\right)+\sum_{k}ms^{out}\left(s_j^{in},k,p\right),$$
$$\forall p\in P,s_j^{in},s_{j'}^{in}\in S_j^{in},k\in K \tag{3.1}$$

$$mw^{out}\left(s_j^{in},p\right)=mw^{e}\left(s_j^{in},p\right)+\sum_{s_j^{in}}mw^{r}\left(s_j^{in},s_{j'}^{in},p\right)+ms^{in}\left(s_j^{in},p\right),$$
$$\forall p\in P,s_j^{in},s_{j'}^{in}\in S_j^{in} \tag{3.2}$$

$$mw^{in}\left(s_j^{in},p\right)=mw^{out}\left(s_j^{in},p\right),\ \ \forall p\in P,s_j^{in},s_{j'}^{in}\in S_j^{in} \tag{3.3}$$

Constraint (3.4) defines the amount of contaminant entering a unit at any given time within slot *p* as the sum of the loads obtained from other processing units and from storage tanks. Constraint (3.5) states that the amount of contaminant leaving a unit is made up of the contaminant load to be removed after a task is processed in a unit and the amount of contaminant in the inlet water stream. It is worth pointing out that the contaminant load to be removed in each unit is modelled as a fraction of the size of the batch that was processed in the unit prior to washing.

$$c^{in}\left(s_j^{in},p\right)mw^{in}\left(s_j^{in},p\right)=\sum_{s_{j'}^{in}}c^{out}\left(s_{j'}^{in},p\right)mw^{r}\left(s_{j'}^{in},s_j^{in},p\right)$$
$$+\sum_{k}cs^{out}(k,p)ms^{out}\left(s_j^{in},k,p\right),$$
$$\forall p\in P,s_j^{in},s_{j'}^{in}\in S_j^{in},k\in K \tag{3.4}$$

$$c^{out}\left(s_j^{in},p\right)mw^{out}\left(s_j^{in},p\right)=M\left(s_j^{in}\right)mu\left(s_j^{in},p\right)+c^{in}\left(s_j^{in},p\right)mw^{in}\left(s_j^{in},p\right),$$
$$\forall p\in P,s_j^{in},s_{j'}^{in}\in S_j^{in} \tag{3.5}$$

Constraints (3.6) and (3.7) ensure that contaminant concentrations of water streams entering and leaving processing units do not exceed their maximum allowable concentrations. Alternatively, Constraint (3.7) can be modified by fixing the outlet concentration of contaminants from each washing operation to its maximum

allowable value. This is usually done in single contaminant problems to ensure that the minimum possible amount of water is used in each operation.

$$c^{in}\left(s_j^{in},p\right)\le C^{in,U}\left(s_j^{in}\right)y\left(s_j^{in},p\right), \qquad \forall p\in P, s_j^{in}\in S_j^{in} \tag{3.6}$$

$$c^{out}\left(s_j^{in},p\right)\le C^{out,U}\left(s_j^{in}\right)y\left(s_j^{in},p\right), \quad \forall p\in P, s_j^{in}\in S_j^{in} \tag{3.7}$$

Constraint (3.8) gives the limiting water requirement for each water operation. It is the amount of water entering an operation at its maximum allowable inlet concentration and exiting the operation at the maximum outlet concentration as illustrated in Figure 3.3. As mentioned earlier, the contaminant load for each operation is not fixed and depends on the batch size. Therefore, the maximum water requirement is determined based on the assumption that the batch size of a specific task occurring in a unit is equal to the capacity of the unit.

$$W^U\left(s_j^{in}\right)=\frac{V_j^U M\left(s_j^{in}\right)}{C^{out,U}\left(s_j^{in}\right)-C^{in,U}\left(s_j^{in}\right)}, \qquad \forall s_j^{in}\in S_j^{in} \tag{3.8}$$

Constraints (3.9), (3.10) and (3.11) ensure that the amount of water entering a unit at any given slot *p* does not exceed the limiting water requirement.

$$mw^{in}\left(s_j^{in},p\right)\le W^U\left(s_j^{in}\right)y\left(s_j^{in},p\right), \qquad \forall p\in P, s_j^{in}\in S_j^{in} \tag{3.9}$$

$$mw^{r}\left(s_{j'}^{in},s_j^{in},p\right)\le W^U\left(s_j^{in}\right)y^{r}\left(s_{j'}^{in},s_j^{in},p\right), \quad \forall p\in P, s_j^{in},s_{j'}^{in}\in S_j^{in} \tag{3.10}$$

$$ms^{out}\left(s_j^{in},k,p\right)\le W^U\left(s_j^{in}\right)ys^{out}\left(s_j^{in},k,p\right), \quad \forall p\in P, s_j^{in}\in S_j^{in}, k\in K \tag{3.11}$$

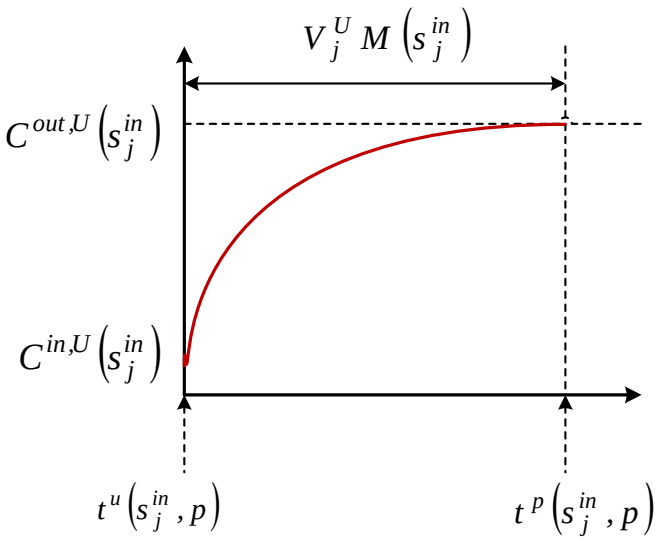


Figure 3.3 *Limiting water requirement for each washing operation (Majozi, 2005a)*

3.3.2 Storage tanks modelling

The material balance around the storage tanks is given in Constraints (3.12) and (3.13). Constraint (3.12) is the water balance around the wastewater storage tank. It states that the amount of water stored at any given time slot *p* is the difference between the amount stored and received from washing operations at the previous time slot and the amount of water discharged to processing units and fed to the regenerator at the current time point. Constraint (3.13) represents the water balance around the diluate storage. It states that the amount of water stored at any given time slot *p* is the amount previously stored and received from the regeneration process at the previous time slot less the amount of water discharged to processing units at the current time slot.

$$qw^s(k,p) = qw^s(k,p-1) + \sum_{s_j^{in}} ms^{in}\left(s_j^{in}, p-1\right) - \sum_{s_j^{in}} ms^{out}\left(s_j^{in}, k, p\right) - mre^{in}(p) \quad , \tag{3.12}$$

$$\forall p \in P, p > p_1, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff}$$

$$qw^s(k,p) = qw^s(k,p-1) + mre^{out}(p-1) - \sum_{s_j^{in}} ms^{out}(s_j^{in},k,p), \quad \forall p \in P, p > p_1, s_j^{in} \in S_j^{in}, k \in K, k = k^{dil} \tag{3.13}$$

Constraints (3.14) and (3.15) illustrate the water balance around storage tanks at the first time slot. Constraints (3.14) states that the amount of water into the wastewater storage at the first time slot is the difference between the amount of water that was initially in storage and the amount of water discharged to processing units and fed into the regenerator. Constraint (3.15) states that the amount of water stored in the diluate storage tank within the first time slot is the amount of water initially stored in the tank at the beginning of the time horizon less the amount of water transferred to processing units for washing operations.

$$qw^s(k,p) = Qw_o^s(k) - \sum_{s_j^{in}} ms^{out}(s_j^{in},k,p) - mre^{in}(p), \quad \forall p \in P, p = p_1, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \tag{3.14}$$

$$qw^s(k,p) = Qw_o^s(k) - \sum_{s_j^{in}} ms^{out}(s_j^{in},k,p), \quad \forall p \in P, p = p_1, s_j^{in} \in S_j^{in}, k \in K, k = k^{dil} \tag{3.15}$$

Constraints (3.16), (3.17) and (3.18) ensure that both storage tanks are empty at the end of the time horizon of interest. This implies that the amount of water stored and partially purified at any given point in time is reused within the time horizon.

$$qw^{s}(k,p)=0, \qquad \forall p\in P, p=|p|, k\in K \tag{3.16}$$

$$\sum_{s_j^{in}} ms^{in}\left(s_j^{in},p\right)=0, \qquad \forall p\in P, p=|p|, s_j^{in}\in S_j^{in} \tag{3.17}$$

$$mre^{out}(p)=0, \qquad \forall p\in P, p=|p| \tag{3.18}$$

Constraint (3.19) is the contaminant balance around the wastewater storage tank. It states that, at any point within slot *p*, the contaminant concentration of water discharge by the tank is made up of the amount of contaminant remaining in storage after discharging water at the previous slot and the amount received from other processing units in the previous slot. Similarly, Constraint (3.20) stipulates the contaminant balance around the diluate storage. It states that the amount of contaminant into the outlet water stream from storage at any slot *p* is the sum of the amount that remained in the amount received from the regenerator in the previous slot. Constraint storage and the (3.21) states that, at the first time slot, the contaminant concentration of the outlet water streams from storage tanks is equal to the concentration of water that was initially found in the tanks at the beginning of the time horizon.

$$cs^{out}(k,p)=\frac{cs^{out}(k,p-1)qw^{s}(k,p-1)+\sum_{s_j^{in}} c^{out}\left(s_j^{in},p\right)ms^{in}\left(s_j^{in},p-1\right)}{qw^{s}(k,p)+\sum_{s_j^{in}} ms^{out}\left(s_j^{in},k,p\right)+mre^{in}(p)} \tag{3.19}$$

$$\forall p\in P, s_j^{in}\in S_j^{in}, k\in K, k=k^{eff}$$

$$cs^{out}(k,p)=\frac{cs^{out}(k,p-1)qw^{s}(k,p-1)+cre^{out}(p)mre^{out}(p-1)}{qw^{s}(k,p)+\sum_{s_j^{in}} ms^{out}\left(s_j^{in},k,p\right)} \tag{3.20}$$

$$\forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{dil}$$

$$cs^{out}(k,p) = Cs_o^{out}(k), \quad \forall p \in P, p = p_1, k \in K \tag{3.21}$$

Constraints (3.22), (3.23) and (3.24) ensure that the amount of water entering and leaving storage tanks does not exceed the upper design bounds of storage tanks.

$$ms^{in}(s_j^{in}, p) \le Qs^U(k) ys^{in}(s_j^{in}, p), \qquad \forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \tag{3.22}$$

$$mre^{in}(p) \le Qs^U(k) y^{re}(p), \qquad \forall p \in P, k \in K, k = k^{eff} \tag{3.23}$$

$$mre^{out}(p) \le Qs^U(k) y^{re}(p), \qquad \forall p \in P, k \in K, k = k^{dil} \tag{3.24}$$

It should be pointed out that the capacity of the storage tanks is not fixed beforehand. Hence Constraints (3.25) - (3.29) ensure that optimum sizes of storage tanks are obtained. Constraints (3.25) and (3.26) ensure that amount of water stored at any point in time does not exceed the optimum tank size. Constraint (3.27) sets upper and lower design bounds for storage capacity. Constraints (3.28) and (3.29) are associated with the existence of storage tanks and ensure that storage exists prior to finding an opportunity to transfer water to storage tanks.

$$v^s(k) \ge qw^s(k,p) + \sum_{s_j^{in}} ms^{in}(s_j^{in}, p), \quad \forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \tag{3.25}$$

$$v^s(k) \ge qw^s(k,p) + mre^{out}(p), \qquad \forall p \in P, k \in K, k = k^{dil} \tag{3.26}$$

$$Qs^L(k) y^s(k) \le v^s(k) \le Qs^U(k) y^s(k), \quad \forall k \in K \tag{3.27}$$

$$y^s(k) \ge ys^{in}(s_j^{in}, p), \qquad \forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \tag{3.28}$$

$$y^s(k) \geq y^{re}(p), \qquad \forall p \in P, k \in K, k = k^{dil} \tag{3.29}$$

3.4 ED design model

A detailed design of the electrodialysis regenerator is considered in this formulation. The model was adapted from the work by Lee et al.(2002) and Tsiakis and Papageorgiou (2005). In this formulation, the Electrodialysis membrane was designed as a single stage process with feed-bleed adopted as the mode of operation as illustrated in Figure 3.4. Constraints (3.30) – (3.50) represent the design equations that characterize the electrodialysis membrane under the following assumptions.

(i) Cocurrent flow for stack operation as shown in Figure 3.4.
(ii) Membrane thickness is neglected.
(iii) The fluid is assumed to be Newtonian and flow to be laminar, incompressible and fully developed.
(iv) Concentrate and diluate compartments have identical geometry for minimum pressure difference, have equal flowrates and similar flow patterns.
(v) Water transport across membranes is negligible when compared to the concentrate and diluate flowrates and concentrations.

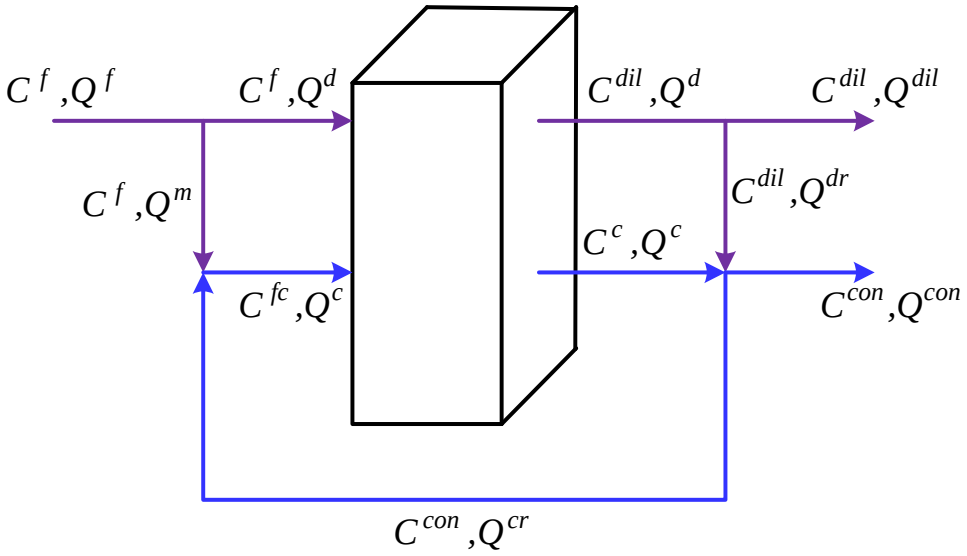


Figure 3.4 *Schematic representation of a single-stage electrodialysis regeneration process*

The material balance around the ED stack follows the schematic representation illustrated in Figure 3.4. The mass balance equations are given by Constraints (3.30) - (3.35). It is worth mentioning that Constraint (3.35) results from abovementioned assumption of identical flowrates in diluate and concentrate compartments.

$$Q^f = Q^{dil} + Q^{con} \tag{3.30}$$

$$Q^f = Q^d + Q^m \tag{3.31}$$

$$Q^d = Q^{dil} + Q^{dr} \tag{3.32}$$

$$Q^c = Q^m + Q^{cr} \tag{3.33}$$

$$Q^{con} = Q^c + Q^{dr} - Q^{cr} \tag{3.34}$$

$$Q^d = Q^c \tag{3.35}$$

The corresponding contaminant balances are given in Constraints (3.36) - (3.39) below.

$$Q^f C^f = Q^{dil} C^{dil} + Q^{con} C^{con} \tag{3.36}$$

$$Q^c C^c + Q^{dr} C^{dil} = Q^{cr} C^{con} + Q^{con} C^{con} \tag{3.37}$$

$$Q^c C^{fc} = Q^m C^f + Q^{cr} C^{cr} \tag{3.38}$$

$$Q^d C^f + Q^c C^{fc} = Q^d C^{dil} + Q^c C^c \tag{3.39}$$

The feed split ratio *m* and the product recovery ratio *r* are given by Constraints (3.40) and (3.41). The feed split ratio determines the ratio between the diluate flowrate and the feed flowrate while the product recovery ratio determines the portion of the diluate flowrate that is recovered as product of the electrodialysis process

$$m = \frac{Q^d}{Q^f} \tag{3.40}$$

$$r = \frac{Q^{dil}}{Q^d} \tag{3.41}$$

Constraint (3.42) is the design equation for the electric current consumed by the electrodialysis stack. It is a function of the electrochemical valence *z*, the Faraday's constant *F*, the flowrate in the diluate compartment Q^d, the degree of desalination C^{Δ}, the current efficiency ε and the number of cell pairs *N*. The degree of desalination defined by Constraint (3.43) is the portion of contaminant transferred from the diluate to the concentrate compartment.

$$I^{el} = \frac{zFQ^{d}C^{\Delta}}{\varepsilon N} \tag{3.42}$$

$$C^{\Delta} = C^{f} - C^{dil} = C^{con} - C^{fc} \tag{3.43}$$

The practical current density has been experimentally proven to be a function of the linear velocity v (Lee, et al., 2013) as shown in Constraint (3.44). The constants a^{LCD} and b^{LCD} in constraint (3.44) are determined experimentally by measuring the limiting current density at various linear velocities (Lee, et al., 2002).

$$i^{prac} = \varsigma a^{LCD} C^{dil} (v)^{b^{LCD}} \tag{3.44}$$

The flowrate in the diluate compartment is determined using the relationship expressed by Constraint (3.45) below. It is a function of the cell thickness δ, the cell width w and the spacer shadow factor α.

$$Q^{d} = N\delta w v \alpha \tag{3.45}$$

In order to achieve a degree of cleanliness through electrodialysis, a total membrane area is required as expressed by Constraint (3.46). The length of the ED stack is defined as a function of the membrane area as shown in constraint (3.47).

$$A = \frac{\left(ln\frac{C^{c}C^{f}}{C^{dil}C^{fc}} + \frac{\psi^{eq}\rho C^{\Delta}}{\delta} \right) zFQ^{d}C^{dil}}{\left(\frac{C^{dil}}{C^{c}} + 1 + \frac{\psi^{eq}C^{\Delta}\rho}{\delta} \right) i^{prac}\beta\varepsilon} \tag{3.46}$$

$$L^{st} = \frac{A}{2wN} \tag{3.47}$$

The direct energy required for the regeneration process is given by Constraint (3.48). It is dependent on the voltage applied to the stack and the current density. The applied voltage is calculated using the relationship given in Constraint (3.49).

$$E^{des} = \frac{U^{st} I^{el}}{Q^{dil}} \tag{3.48}$$

$$U^{st} = \frac{Q^{d} C^{\Delta} zFN}{\varepsilon A}\left(\frac{ln \frac{c^{c} c_{reg}^{f}}{c_{reg}^{dil} c^{fc}}}{\psi^{eq} C^{\Delta}} + \rho \right) \tag{3.49}$$

Constraint (3.50) gives the mathematical expression for the energy required for pumping the feed into the ED stack. It is a function of the pressure drop across the stack and the pump efficiency. The pressure drop across the ED unit is expressed using the relationship shown by Constraint (3.51) assuming a laminar flowrate.

$$E^{pu} = \frac{\Delta P^{st} k^{tr}}{\eta_p} \tag{3.50}$$

$$\Delta P^{st} = \frac{12 v \mu L^{st}}{\delta^2} \tag{3.51}$$

The regenerator is modelled to operate semi-continuously at constant flowrate within the time horizon. Constraints (3.52) and (3.53) link the amount of wastewater fed to the regenerator to its actual feed flowrate. They ensure that the amount of water transferred from storage to the regenerator at slot *p* is equal to the total quantity of water fed into the ED for the duration regeneration process at time slot *p*. These

constraints are only valid if the regenerator is active at time slot *p* and become redundant otherwise.

$$mre^{in}(p) \le Q^{f}\tau^{re}(p) + Qs^{U}(k)\left(1 - y^{re}(p)\right), \qquad \forall p \in P, k \in K, k = k^{eff} \tag{3.52}$$

$$mre^{in}(p) \ge Q^{f}\tau^{re}(p) - Qs^{U}(k)\left(1 - y^{re}(p)\right), \qquad \forall p \in P, k \in K, k = k^{eff} \tag{3.53}$$

Similarly, Constraints (3.54) and (3.55) ensure that the total amount of water discharged into the diluate tank at slot *p* is equal to the total amount of regenerated water that flowed out of the regenerator for the period within which it was active at slot *p*.

$$mre^{out}(p) \le Q^{dil}\tau^{re}(p) + Qs^{U}(k)\left(1 - y^{re}(p)\right), \qquad \forall p \in P, k \in K, k = k^{dil} \tag{3.54}$$

$$mre^{out}(p) \ge Q^{dil}\tau^{re}(p) - Qs^{U}(k)\left(1 - y^{re}(p)\right), \qquad \forall p \in P, k \in K, k = k^{dil} \tag{3.55}$$

Constraints (3.56) and (3.57) together ensure that the contaminant level of water discharged from the wastewater storage at slot *p* is the same as the level of contaminants in the inlet stream to the ED unit. These constraints are only valid when the regenerator is active at a given slot *p*.

$$\begin{aligned} &cs^{out}(k,p) \le C^{f} + \max_{s_j^{in}}\left(C^{out,U}\left(s_j^{in}\right)\right)\left(1 - y^{re}(p)\right), \\ &\forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \end{aligned} \tag{3.56}$$

$$\begin{aligned} &cs^{out}(k,p) \ge C^{f} - \max_{s_j^{in}}\left(C^{out,U}\left(s_j^{in}\right)\right)\left(1 - y^{re}(p)\right), \\ &\forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \end{aligned} \tag{3.57}$$

Similarly, Constraints (3.58) and (3.59) ensure that both the diluate stream flowing out of the regenerator and the amount of water entering the diluate storage tank at

time slot *p* have the same contaminant level. Again, the constraints hold only if the regenerator is active at slot *p*, i.e. $y^{re}(p)=1$.

$$cre^{out}(p) \le C^{dil} + \max_{s_j^{in}}\left(C^{out,U}\left(s_j^{in}\right)\right)\left(1-y^{re}(p)\right), \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.58}$$

$$cre^{out}(p) \ge C^{dil} - \max_{s_j^{in}}\left(C^{out,U}\left(s_j^{in}\right)\right)\left(1-y^{re}(p)\right), \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.59}$$

3.5 Sequencing constraints for water network

This section consists of a set of constraints formulated to ensure that the discrete nature of batch processes is captured, i.e. adequate sequencing of different events and tasks within a given time horizon of interest.

In this formulation, water is used as a cleaning agent in washing operations which occur after a task has been processed in a unit. Constraints (3.60) - (3.62) consist of the sequencing constraints between batch tasks and washing operations. Constraint (3.60) states that the duration of washing is the difference between the starting and finishing time of a washing operation in a unit. Constraint (3.61) ensures that a washing operation starts after the corresponding task is completed in a processing unit. Constraint (3.62) states that a batch operation can start within slot *p* after the completion of the washing operation at the previous time slot.

$$tw^{p}\left(s_j^{in}, p\right) = tw^{u}\left(s_j^{in}, p\right) + \tau^{w}\left(s_j^{in}\right) y\left(s_j^{in}, p\right), \quad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.60}$$

$$tw^{u}\left(s_j^{in}, p\right) \ge t^{p}\left(s_j^{in}, p\right), \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.61}$$

$$t^{u}\left(s_j^{in}, p\right) \ge tw^{p}\left(s_j^{in}, p-1\right), \quad \forall p \in P, p > p_1, s_j^{in} \in S_j^{in} \tag{3.62}$$

As mentioned earlier, this formulation explores both direct and indirect reuse opportunities within a multipurpose batch plant. Constraints (3.63) – (3.65) describe

the conditions to be fulfilled for direct reuse of water to occur between two processing units. Constraint (3.63) states that for direct reuse to occur between two washing operations, the operation receiving water must first take place, but the task can still occur when no direct opportunities are found. Constraint (3.64) and (3.65) together ensure that the finishing time of the task discharging water and the starting time of the task receiving water coincide for direct reuse to occur.

$$y^r\left(s_{j'}^{in}, s_j^{in}, p\right) \le y\left(s_j^{in}, p\right), \ \forall p \in P, s_j^{in}, s_{j'}^{in} \in S_j^{in} \tag{3.63}$$

$$tw^p\left(s_j^{in}, p\right) \ge tw^u\left(s_j^{in}, p\right) - H\left(1 - y^r\left(s_{j'}^{in}, s_j^{in}, p\right)\right), \ \forall p \in P, s_j^{in}, s_{j'}^{in} \in S_j^{in} \tag{3.64}$$

$$tw^p\left(s_j^{in}, p\right) \le tw^u\left(s_j^{in}, p\right) + H\left(1 - y^r\left(s_{j'}^{in}, s_j^{in}, p\right)\right), \ \forall p \in P, s_j^{in}, s_{j'}^{in} \in S_j^{in} \tag{3.65}$$

Constraint (3.66) states that a washing operation must be scheduled to take place prior to water being discharged from storage vessels to processing units. However, the occurrence of a washing operation does not depend on whether an indirect reuse opportunity is found at any given time slot *p*. Constraints (3.67) and (3.68) work together to ensure that the time at which water is discharged from storage to a processing unit coincides with the starting time of the washing operation in that unit.

$$ys^{out}\left(s_j^{in}, k, p\right) \le y\left(s_j^{in}, p\right), \ \forall p \in P, s_j^{in} \in S_j^{in}, k \in K \tag{3.66}$$

$$ts^{out}\left(s_j^{in}, k, p\right) \le tw^u\left(s_j^{in}, p\right) + H\left(1 - ys^{out}\left(s_j^{in}, k, p\right)\right), \quad \forall p \in P, s_j^{in} \in S_j^{in}, k \in K \tag{3.67}$$

$$ts^{out}\left(s_j^{in}, k, p\right) \ge tw^u\left(s_j^{in}, p\right) - H\left(1 - ys^{out}\left(s_j^{in}, k, p\right)\right), \quad \forall p \in P, s_j^{in} \in S_j^{in}, k \in K \tag{3.68}$$

Constraint (3.69), similar to Constraint (3.66), states that the existence of an opportunity to transfer water from washing operations to the wastewater tank depends

on the occurrence of washing operations. Constraints (3.70) and (3.71) state that the transfer time should be equal to the finishing time of the washing task for water to be transferred from a processing unit to storage.

$$ys^{in}\left(s_j^{in},p\right)\le y\left(s_j^{in},p\right), \qquad \forall p\in P, s_j^{in}\in S_j^{in} \tag{3.69}$$

$$ts^{in}\left(s_j^{in},p\right)\le tw^{p}\left(s_j^{in},p\right)+H\left(1-ys^{in}\left(s_j^{in},p\right)\right), \quad \forall p\in P, s_j^{in}\in S_j^{in} \tag{3.70}$$

$$ts^{in}\left(s_j^{in},p\right)\ge tw^{p}\left(s_j^{in},p\right)-H\left(1-ys^{in}\left(s_j^{in},p\right)\right), \quad \forall p\in P, s_j^{in}\in S_j^{in} \tag{3.71}$$

Constraints (3.72) and (3.73) state that, if there are opportunities for water to be discharged from storage to different processing units at the same time slot *p*, the discharge time should be the same. These constraints ensure that all the streams leaving storage have the same contaminant concentration at any given point within time slot *p*. Constraint (3.74) ensures that the discharge time of water from storage to processing units at earlier time slots is earlier than the discharge time at later time slots.

$$\begin{aligned} &ts^{out}\left(s_j^{in},k,p\right)\le ts^{out}\left(s_{j'}^{in},k,p\right) \\ &+H\left(2-ys^{out}\left(s_j^{in},k,p\right)-ys^{out}\left(s_{j'}^{in},k,p\right)\right), \forall p\in P, s_j^{in},s_{j'}^{in}\in S_j^{in}, k\in K \end{aligned} \tag{3.72}$$

$$\begin{aligned} &ts^{out}\left(s_j^{in},k,p\right)\ge ts^{out}\left(s_{j'}^{in},k,p\right) \\ &-H\left(2-ys^{out}\left(s_j^{in},k,p\right)-ys^{out}\left(s_{j'}^{in},k,p\right)\right), \forall p\in P, s_j^{in},s_{j'}^{in}\in S_j^{in}, k\in K \end{aligned} \tag{3.73}$$

$$\begin{aligned} &ts^{out}\left(s_j^{in},k,p\right)\ge ts^{out}\left(s_{j'}^{in},k,p'\right)-H\left(2-ys^{out}\left(s_j^{in},k,p\right)-ys^{out}\left(s_{j'}^{in},k,p'\right)\right) \\ &, \forall p,p'\in P, p'\le p, s_j^{in},s_{j'}^{in}\in S_j^{in}, k\in K \end{aligned} \tag{3.74}$$

Constraints (3.75), (3.76) and (3.77) are similar to constraints (3.72), (3.73) and (3.74) respectively, but apply to opportunities where water is transferred from processing units to storage.

$$ts^{in}\left(s_j^{in},p\right)\le ts^{in}\left(s_{j'}^{in},p\right)+H\left(2-ys^{in}\left(s_j^{in},p\right)-ys^{in}\left(s_{j'}^{in},p\right)\right),\quad \forall p\in P, s_j^{in}, s_{j'}^{in}\in S_j^{in} \tag{3.75}$$

$$ts^{in}\left(s_j^{in},p\right)\ge ts^{in}\left(s_{j'}^{in},p\right)-H\left(2-ys^{in}\left(s_j^{in},p\right)-ys^{in}\left(s_{j'}^{in},p\right)\right),\quad \forall p\in P, s_j^{in}, s_{j'}^{in}\in S_j^{in} \tag{3.76}$$

$$ts^{in}\left(s_j^{in},p\right)\ge ts^{in}\left(s_{j'}^{in},p'\right)-H\left(2-ys^{in}\left(s_j^{in},p\right)-ys^{in}\left(s_{j'}^{in},p'\right)\right),\quad \forall p,p'\in P, p'\le p, s_j^{in}, s_{j'}^{in}\in S_j^{in} \tag{3.77}$$

Constraint (3.78) suppresses the opportunities for a storage tank to discharge and receive water to and from different units at the same time slot. This is due to the fact that the concentration of the outlet stream from storage at any given slot does not cater for inlet streams within the slot. Constraint (3.79) states that opportunities to transfer water from storage to processing units at earlier time slots *p'* should occur earlier than opportunities for the storage tank to receive water from processing units at later time slots *p*. This constraint only holds when the described opportunities are found during optimization, i.e. $ys^{in}(s_j^{in},p)=1$ and $ys^{out}(s_{j'}^{in},k,p')=1$.

$$ys^{in}\left(s_j^{in},p\right)+ys^{out}\left(s_{j'}^{in},k,p\right)=1,\quad \forall p\in P, s_j^{in}, s_{j'}^{in}\in S_j^{in}, k\in K \tag{3.78}$$

$$ts^{in}\left(s_j^{in},p\right)\ge ts^{out}\left(s_{j'}^{in},k,p'\right)-H\left(2-ys^{in}\left(s_j^{in},p\right)-ys^{out}\left(s_{j'}^{in},k,p'\right)\right),\quad \forall p,p'\in P, p'\le p, s_j^{in}, s_{j'}^{in}\in S_j^{in}, k\in K \tag{3.79}$$

The regenerator, which operates semi-continuously, receives and discharges water from and to a storage tank. In order to know the time at which water starts being fed

to the electrodialysis process and the time at which a portion of the diluate is available for reuse in the diluate storage, the regenerator operation was discretized into time slots of unknown duration as shown in Figure 3.5.

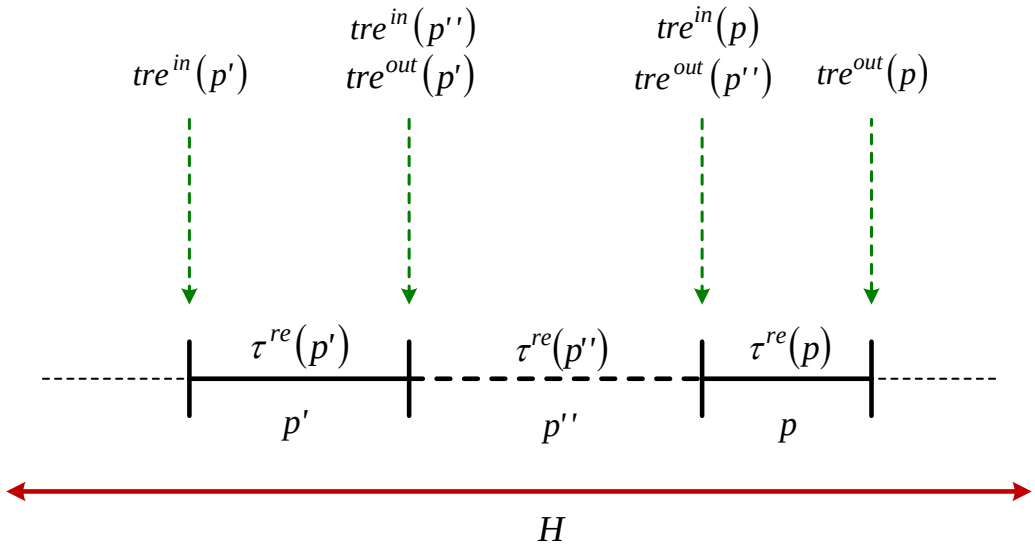


Figure 3.5 *Modelling technique for the regenerator operation*

Constraint (3.80) gives the duration of time slot p within which the regeneration process is active. The extreme ends of each time slot coincide with the starting and finishing time of the process as shown in Figure 7. Constraints (3.81) and (3.82) together state that the finishing time and starting time of the electrodialysis process at two consecutive time slots should coincide to ensure semi-continuous operation of the process shown in Figure 7. Constraint (3.83) ensures that the regeneration process occurs within the time horizon of interest.

$$tre^{out}(p) = tre^{in}(p) + \tau^{re}(p) y^{re}(p), \quad \forall p \in P \tag{3.80}$$

$$tre^{in}(p) \le tre^{out}(p') + H\left(2 - y^{re}(p) - y^{re}(p') + \sum_{p''} y^{re}(p'')\right), \tag{3.81}$$

$$\forall p, p'', p' \in P, p > p'' > p'$$

$$tre^{in}(p) \geq tre^{out}(p') - H\left(2 - y^{re}(p) - y^{re}(p') + \sum_{p''} y^{re}(p'')\right), \quad (3.82)$$

$$\forall p, p'', p' \in P, p > p'' > p'$$

$$\sum_{p} \tau^{re}(p) \leq H, \ \forall p \in P \quad (3.83)$$

Constraint (3.84), similarly to constraint (3.78), ensures that the wastewater storage does not receive water from processing unit and feed water to the ED unit within the same time slot. Constraint (3.85) states that the time at which the regeneration process starts within time slot *p* should be later than the time at which the wastewater storage received water from processing units at previous time slots *p'*.

$$y^{re}(p) + ys^{in}(s_j^{in}, p) = 1, \ \forall p \in P, s_j^{in} \in S_j^{in} \quad (3.84)$$

$$tre^{in}(p) \geq ts^{in}(s_j^{in}, p') - H\left(2 - y^{re}(p) - ys^{in}(s_j^{in}, p')\right), \quad \forall p, p' \in P, p' \leq p, s_j^{in} \in S_j^{in} \quad (3.85)$$

Constraints (3.86) and (3.87) ensure that the wastewater storage tank discharges water to processing units and feeds water to the regenerator at the same time if both events occur within the same time slot *p*. Constraint (3.88) states that the discharge time of water from storage to processing units at a previous time slot *p'* should be earlier than the time at which water is fed into the regenerator at a later time slot *p*.

$$tre^{in}(p) \leq ts^{out}(s_j^{in}, k, p) + H\left(2 - y^{re}(p) - ys^{out}(s_j^{in}, k, p)\right), \quad \forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \quad (3.86)$$

$$tre^{in}(p) \geq ts^{out}\left(s_j^{in},k,p\right) - H\left(2 - y^{re}(p) - \left(ys^{out}s_j^{in},k,p\right)\right), \quad \forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \tag{3.87}$$

$$tre^{in}(p) \geq ts^{out}\left(s_j^{in},k,p'\right) + H\left(2 - y^{re}(p) - ys^{out}\left(s_j^{in},k,p'\right)\right), \quad \forall p,p' \in P, p' \leq p, s_j^{in} \in S_j^{in}, k \in K, k = k^{eff} \tag{3.88}$$

Constraint (3.89) states that the diluate storage tank cannot discharge water to washing operations and receive water from the regenerator within the same time slot *p*. Constraint (3.90) ensures that the transfer of water from the regenerator to the diluate tank at an earlier time slot *p'* occur earlier than the discharge of water from the tank to washing operations at a later slot *p*.

$$y^{re}(p) + ys^{out}\left(s_j^{in},k,p\right) = 1, \forall p \in P, s_j^{in} \in S_j^{in}, k \in K, k = k^{dil} \tag{3.89}$$

$$ts^{out}\left(s_j^{in},k,p\right) \geq tre^{out}(p') - H\left(2 - y^{re}(p') - ys^{out}\left(s_j^{in},k,p\right)\right), \quad \forall p,p' \in P, p' \leq p, s_j^{in} \in S_j^{in}, k \in K, k = k^{dil} \tag{3.90}$$

Constraints (3.91) – (3.98) ensure that every task, event and process integration opportunity within the plant occur within the time horizon of interest.

$$t^{u}\left(s_j^{in},p\right) \leq H, \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.91}$$

$$t^{p}\left(s_j^{in},p\right) \leq H, \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.92}$$

$$tw^{u}\left(s_j^{in},p\right) \leq H, \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.93}$$

$$tw^{p}\left(s_j^{in},p\right) \leq H, \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.94}$$

$$ts^{in}\left(s_j^{in},p\right) \leq H, \qquad \forall p \in P, s_j^{in} \in S_j^{in} \tag{3.95}$$

$$ts^{out}\left(s_j^{in},k,p\right)\le H\,, \qquad \forall p\in P, s_j^{in}\in S_j^{in}, k\in K \tag{3.96}$$

$$tre^{in}\left(p\right)\le H\,, \qquad \forall \boldsymbol{p}\in \boldsymbol{P} \tag{3.97}$$

$$tre^{out}\left(p\right)\le H\,, \qquad \forall \boldsymbol{p}\in \boldsymbol{P} \tag{3.98}$$

3.6 Objective function

The objective function of this formulation consists of maximizing the annualized plant profit as illustrated by Constraint (3.99). It takes into account the production revenue, the costs of freshwater and wastewater disposal, the capital and operating costs of ED unit, as well as the installation and capital cost of storage tanks used.

$$max\left(\begin{array}{l}\left[\begin{array}{l}\sum_{s_p} SP\left(s_p\right)qs\left(s_p\right)\\ -C^{fw}\sum_{p}\sum_{s_j^{in}} mw^{f}\left(s_j^{in},p\right)-C^{ew}\sum_{p}\sum_{s_j^{in}} mw^{e}\left(s_j^{in},p\right)+Q^{con}\tau^{re}\left(p\right)\end{array}\right]\frac{t^d}{H}\\ -\frac{C^{mb}}{t^{max}}A+\sum_{p}\tau^{re}(p)\frac{t^d C^{el}Q^{dil}}{H}\left(E^{des}+E^{pu}\right)\\ -\frac{1}{t^{max}}\sum_{k}C^{fst}y^{s}\left(k\right)+C^{vst}\left(v^{s,U}\right)^{n}\end{array}\right) \tag{3.99}$$

3.7 Nomenclature

The formulated mathematical model uses the following sets, parameters and variables.

Sets

P { $p \mid p$ represents a time point}

J	$\{ j \mid j$ denotes a unit$\}$
S_j^{in}	$\{ s_j^{in} \mid s_j^{in}$ is an effective state representing a task performed in unit $j\}$
K	$\{ k \mid k$ is a storage tank$\}$
S_P	$\{ s_p \mid s_p$ is state representing a product$\}$

Parameters

V_j^U	capacity of unit j
H	time horizon of interest
$SP(s_p)$	selling price of product
$\tau(s_j^{in})$	duration of a processing task in unit j
$\tau^w(s_j^{in})$	duration of washing in unit j
$C^{out,U}(s_j^{in})$	maximum allowable outlet concentration of water from unit j
$C^{in,U}(s_j^{in})$	maximum allowable concentration of water entering unit j
$M(s_j^{in})$	mass load of contaminant to be removed in unit j
$Qs^U(k)$	maximum amount of water that can be stored in storage tank k
$Qs^L(k)$	minimum amount of water that can be stored in storage tank k
$Qw_o^s(k)$	initial amount of water stored in storage tank k
$Cs_o^{out}(k)$	initial concentration of water stored in storage tank k
$W^U(s_j^{in})$	limiting water requirement in unit j
C^{fw}	freshwater cost in c.u/kg
C^{ew}	cost of wastewater treatment in c.u/kg
$Cs_o^{out}(k)$	initial concentration of water in storage k
a^{LCD}	constant for the limiting current density
b^{LCD}	constant for the limiting current density
F	faraday constant

C^{el}	electric power cost (c.u./kWh)
C^{mb}	membrane capital cost (c.u/m^2)
C^{fst}	installation cost of storage tanks (c.u)
C^{vst}	purchased cost of storage tanks (c.u/kg)
η	cost coefficient of storage tanks
k^{tr}	conversion factor
ς	safety factor
t^{max}	estimated maximum membrane equipment life
t^{d}	total operating time per year
W	width of electrodialysis cell
z	electrochemical valence
α	effective volume of cell factor (spacer)
β	effective area of cell factor (spacer shadow)
δ	thickness of an electrodialysis cell
ε	current utilization
η_p	pump efficiency
μ	viscosity of water
ρ	total resistance of anionic and cationic exchange membrane
ψ^{eq}	equivalent conductance of water
rr	removal ration of contaminant during regeneration process
M^{mol}	molecular mass of contaminant

Continuous Variables

$mu\left(s_j^{in}, p\right)$	amount of material processed by a task at time slot *p*
$mw^{in}\left(s_j^{in}, p\right)$	amount of water entering a unit at time slot *p*
$mw^{out}\left(s_j^{in}, p\right)$	amount of water entering a unit at time slot *p*
$mw^{r}\left(s_j^{in}, s_{j'}^{in}, p\right)$	amount of water reused from unit *j* to *j'* at time slot *p*
$mw^{e}\left(s_j^{in}, p\right)$	amount of water sent from unit *j* to effluent at time slot *p*

$mw^{f}\left(s_j^{in},p\right)$	amount of freshwater used in unit *j* at time slot *p*
$ms^{in}\left(s_j^{in},p\right)$	amount of water transferred from unit *j* to storage at time slot *p*
$ms^{out}\left(s_j^{in},k,p\right)$	amount of water transferred from storage *k* to unit *j* at time slot *p*
$mre^{in}(p)$	amount of water transferred from storage to the regenerator at time slot *p*
$mre^{out}(p)$	amount of water transferred from regenerator to storage at time slot *p*
$qs\left(s_p,p\right)$	amount of product stored at time slot *p*
$qw^{s}(k,p)$	amount of water stored in storage tank *k* at time slot *p*
$c^{in}\left(s_j^{in},p\right)$	concentration of water entering unit *j* at time slot *p*
$c^{out}\left(s_j^{in},p\right)$	concentration of water leaving unit *j* at time slot *p*
$cs^{out}\left(k,p\right)$	concentration of water leaving storage tank *k* at time slot *p*
$cre^{out}\left(p\right)$	concentration of water leaving the regenerator at time slot *p*
$t^{u}\left(s_j^{in},p\right)$	starting time of a task at time slot *p*
$t^{p}\left(s_j^{in},p\right)$	finishing time of a task at time slot *p*
$tw^{u}\left(s_j^{in},p\right)$	starting time of washing task at time slot *p*
$tw^{p}\left(s_j^{in},p\right)$	finishing time of washing task at time slot *p*
$ts^{in}\left(s_j^{in},p\right)$	transfer time of from a unit to storage at time slot *p*
$ts^{out}\left(s_j^{in},k,p\right)$	transfer time of water from storage tank *k* to unit *j* at time slot *p*
$tre^{in}\left(p\right)$	transfer time of water from storage to regenerator at time slot *p*
$tre^{out}\left(p\right)$	transfer time of water from the regenerator to storage tank at time slot *p*
$\tau^{re}(p)$	duration of regeneration process at time slot *p*

$v^s(k)$	design capacity of storage tank *k*
A	total membrane area required for desalination
Q^f	inlet feed flowrate to the regenerator
Q^{dil}	diluate product flowrate
Q^{con}	concentrate product flowrate
Q^d	diluate stream flowrate
Q^c	concentrate stream flowrate
Q^m	feed split flowrate
Q^{dr}	diluate recycle stream flowrate
Q^{cr}	concentrate recycle stream flowrate
C^f	concentration of inlet feed stream to the regenerator
C^{dil}	outlet concentration of diluate stream
C^{con}	outlet concentration of concentrate stream
C^{fc}	inlet concentration of concentrate stream
C^c	concentration of outlet concentrate compartment stream
C^{cr}	concentration of concentrate recycle stream
E^{des}	specific desalination energy required by regenerator
E^{pu}	pumping energy required by regenerator
I^{el}	electric current required by regenerator
i^{prac}	practical limiting current density
L^{st}	ED stack length
m	ED feed split rate
r	ED diluate product recovery rate
v	linear ED flow velocity
U^{st}	voltage applied to the ED stack
ΔP^{st}	pressure drop across the ED stack

Integer variables

N	number of cell pairs required for desalination

Binary variables

$y\left(s_j^{in}, p\right)$	binary variable associated with the assignment of a task at time slot *p*
$y^r\left(s_j^{in}, s_{j'}^{in}, p\right)$	binary variable associated with the existence of a direct reuse stream from *j* to *j'* at time slot *p*
$y^{re}(p)$	binary variable associated with the existence of regeneration process at time slot *p*
$ys^{in}\left(s_j^{in}, p\right)$	binary variable associated with the transfer of water from unit *j* to storage time slot *p*
$ys^{out}\left(s_j^{in}, k, p\right)$	binary variable associated with the transfer of water from storage to unit *j*
$y^s\left(k\right)$	binary variable associated with the existence of a storage tank *k*

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4

ILLUSTRATIVE EXAMPLES

4.1 Introduction

The developed formulation was applied to two literature examples for verification and practicability analysis. The resultant models for both examples were implemented in GAMS 24.3.3 and solved using BARON. The computer used to solve the models had the following specifications: Windows 7 Professional, Intel(R) Core ™ i7-4770 CPU @ 3.40GHz, 8.00 GB, and 64-bit Operating System.

4.2 Case study I

The first case study used for the verification of this formulation was adapted from Halim and Srinivasan (2011). It is a simple batch plant that manufactures chemical D using raw material A following the process illustrated in Figure 4.1. The production line involves 3 tasks occurring in 5 units. Task 1 can be performed in units 1 and 2, task 2 in unit 3 and task 3 in units 4 and 5. The operational philosophy of the plant requires units 1, 2, 4 and 5 to be washed before the next batch is processed. Water is used as a cleaning medium for the removal of residues remaining after processing a task in a unit. Table 4.1 and Table 4.2 give a set of input parameters required for the scheduling of the process. The information includes the available units and their corresponding tasks, the processing time and washing time for each task, the amount of raw material available in the plant, the storage capacity of raw materials,

intermediate materials and products, the selling price of products, as well as freshwater cost and wastewater disposal costs. The duration of each task, i.e., processing time, is fixed and independent of the batch size as shown in Table 4.1.

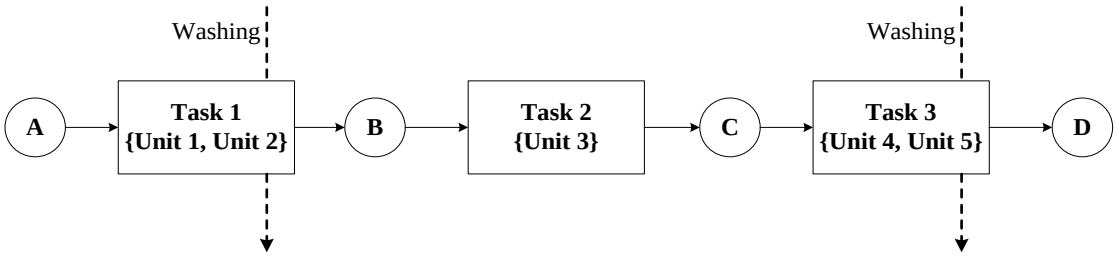


Figure 4.1 *State task network representation of the production recipe for case study I*

Table 4.3 gives a set of data pertaining to water integration for different tasks in their respective units. This includes the maximum inlet and outlet contaminant water concentrations as well as the contaminant mass load. The contaminant to be removed in this case is sodium chloride (NaCl). It can be seen that task 2 occurring in unit 2 does not require washing; this explains why there is no data for maximum inlet and outlet contaminant concentration for this task. Table 4.4 contains the parameters for the design and costing of the ED unit and the storage tanks. The ED design and costing input parameters were directly obtained from Tsiakis and Papageorgiou (2005) while the costing parameters of a carbon steel storage tank were obtained from Li and Chang (2006).The Chemical Engineering Plant Cost Index (CEPCI) was used to account for the effect of years on the capital cost of storage tanks. The case study focuses on a time horizon of 12h for short-term scheduling of the given plant.

Table 4.1 *Production scheduling data for case study I*

Units	Suitability	Maximum batch size (kg)	Processing time (h)	Washing time (h)
Unit 1	Task 1	100	1.25	0.25
Unit 2	Task 1	150	1.7	0.30
Unit 3	Task 2	200	1.5	0.00
Unit 4	Task 3	100	0.75	0.25
Unit 5	Task 3	150	1.2	0.30

Table 4.2 *Additional scheduling data for case study I*

Material state	Initial inventory	Max storage (kg)	Revenue or cost (c.u/kg)
A	1000	1000	0
B	0	200	0
C	0	200	0
D	0	1000	5
Freshwater	-	200	0.1
Wastewater	-	150	0.05

Table 4.3 *Process integration data for washing tasks in case study I*

Units	Suitability	Max inlet concentration (ppm)	Max outlet concentration (ppm)	Contaminant loading (g NaCl/kg batch)
Unit 1	Task 1	500	1000	0.2
Unit 2	Task 1	50	100	0.2
Unit 3	Task 2	-	-	-
Unit 4	Task 3	150	300	0.2
Unit 5	Task 3	300	2000	0.2

Table 4.4 *Additional parameters for the design and costing of the ED unit and storage tanks for case study I and II*

Parameters	**Symbols**	**Value**
Limiting current density constant	a^{LCD}	2500
Limiting current density constant	b^{LCD}	0.5
Faraday's constant, A s/keq	F	96,500,000
Conversion factor, kWh/J	k^{tr}	27.2
Safety factor	ς	0.7
Cell width, m	w	0.42
Cell thickness, m	δ	0.00065
Effective volume of cell factor (spacer)	α	0.8
Effective cell factor volume (spacer shadow)	β	0.7
Current utilization	ε	0.9
Pump efficiency	η_p	0.7
Solution viscosity, kg/ m s	μ	0.000984
Total resistance of membranes, Ω m^2	ρ	0.0007
Equivalent conductance of solutions, s m^2/keq	ψ^{eq}	10.5
Contaminant removal ratio	rr	0.95
Membrane capital cost, c.u./m^2	C^{mb}	150
Electric power cost, c.u./kWh	C^{el}	0.12
Storage tank fixed cost , c.u.	C^{fst}	50,000
Storage tank purchased cost, c.u./kg	C^{vst}	280
Storage tank cost coefficient	n	0.6
Estimated maximum equipment life, y	t^{max}	5
Operating time per year, s	t^{d}	28,512,000

4.2.1 Computational results and discussion

The solution of the formulation yielded the plant schedule as shown in Figure 4.2. Figure 4.2 shows the optimum sequence of batch processing tasks and their subsequent washing operations from unit 1 to unit 5. It also shows the resultant water network where different arrows illustrate different opportunities for water reuse as well as freshwater streams. For example, the second washing operation in unit 2 received 190.8kg from the freshwater source and the same amount from the wastewater storage tank. At the end of the operation, 204.2 kg of wastewater was then sent to the wastewater storage tank for later reuse and the remaining amount, i.e. 177.4 kg, was discharged as effluent. The optimum feed, diluate and concentrate flowrates around the ED regenerator were found to be 100.8 kg/h, 95.8 kg/h, and 5 kg/h respectively. The sizes of batch processing tasks in each unit are also displayed in Figure 4.2. Illustratively, unit 1 processed 6 batches of 100 kg each, while unit 2 processed 4 batches of 104.6 kg, 95.4 kg, 100 kg and 100 kg respectively. The wastewater reusable storage and the diluate storage were found to have optimum sizes of 222.6 kg and 189.8 kg respectively.

From Table 4.3, it can be observed that washing operations in unit 2 have the lowest inlet and outlet contaminant restrictions. As a result, effluents from unit 2 are easily reused in all other units but effluents from the other 3 units are not directly or indirectly reused to unit 2 without purification or dilution. Therefore, the regenerator is operated continuously for 2h in order to partially purify a portion of wastewater and facilitate reuse in unit 2. The model also found opportunities for wastewater from the wastewater storage to be diluted with freshwater and reuse in unit 2 as a way of minimizing freshwater use and the cost of wastewater regeneration.

Table 4.5 gives a comparative study between the results obtained from a base case model with those obtained using the proposed formulation. The base case model includes constraints pertaining to scheduling and water balance. It considers freshwater as the only available water source to satisfy all water-using operations.

This implies that no reuse opportunity for water is explored among processing units. It can be seen from Table 4.5 that the proposed formulation allowed the plant to save 37.4 % of the initial amount of freshwater used when no integration was employed. However, the CPU time drastically increased from 0.2 to 28,782 seconds. This is explained by the higher number of constraints, variables and nonlinear terms that the resultant formulation entails as shown in Table 4.5.

Table 4.5 *Comparative results for case study I*

	No integration	**Proposed formulation**
Annual Profit (c.u×10^5)	-	32.3
Freshwater (kg)	1,105	691.2
Revenue (c.u) for 12h horizon	5,000	5,000
Percentage freshwater saving	-	37.4
No. constraints	905	5,295
No. variables	555	1,486
No. discrete variables	75	348
No. binary variables	75	248
Non-linear terms	64	998
CPU time (s)	0.32	28,782

The complexity of the resulting model is explained by the fact that the model attempts to synthesize a water network while designing the regeneration process and optimizing the schedule of the plant. Hence the formulation is more suited for the design phase of the batch plant. However, the operation phase will reduce the problem to a synthesis problem and further simplification can occur for processes where the schedule of the plant is not subject to change. Table 4.6 gives the design parameters pertaining to the regenerator suitable for the process described in this case

study. It includes the total membrane area required for the resultant plant set up, the number of cell pairs in the ED stack, the length of the stack, etc. The total pumping and desalination energy required for the process are also given in Table 4.6.

Table 4.6 *Design specifications of the ED regenerator for case study I*

Design variables	**Optimum values**
Membrane area(m^2)	7.1
No. cell pairs	12
ED stack length(m)	0.7
Desalination energy (kWh/y)	3.632
Pumping energy (kWh/y)	0.078
Electric current (A)	0.651
Product recovery rate	0.95
Linear velocity(m/s)	0.011

The implication of implementing a detailed regeneration model as opposed to adopting a black-box approach was investigated. Table 4.7 compares the results obtained from the proposed mathematical formulation with an embedded ED model to those obtained when the ED model is replaced with a black-box regenerator model. The black-box model used the same removal ratio and liquid recovery as the ED design model. The case where the objective function of the black-box formulation does not include the regeneration cost was considered in the presented black-box approach. It can be seen, from Table 4.7, that the black-box approach achieved 57.5 % reduction in freshwater consumption as opposed to the 37.4 % achieved by the proposed formulation. However, the higher reduction in freshwater consumption entailed an increase in the amount of water fed to the regenerator unit, in the duration of the regenerator operation within the makespan, in the total amount of energy consumption, and in the size of storage tanks. As a result, a 13.3 % reduction in the total cost of the water network was observed when adopting the proposed formulation

as opposed to the black-box approach. The total cost of water network as given in Table 4.7 accounted for the cost of freshwater, the cost of wastewater treatment and disposal, the capital and operating cost of regeneration and the cost of storage. The production revenue was not included in the cost analysis because it was kept at its maximum value in both approaches.

The total energy consumed by the regenerator when adopting the black-box approach was obtained by performing a two-step optimization. Firstly, the black-box model was solved wherein the plant profit was maximized by considering the production revenue, the freshwater and wastewater cost. The second step consisted of optimizing the capital and operational cost of regeneration using the electrodialysis standalone model. The flowrates and contaminant concentrations around the regenerator were fixed to the value obtained in the first step. The total energy consumption of the regenerator within the time horizon was then calculated. A comparison between the results obtained from this technique and the proposed optimization approach shows that a 31.6 % reduction in energy consumption was achieved when adopting the proposed formulation instead of using the black-box modelling approach.

Table 4.7 *Results from black-box and detailed modelling approaches*

	Black-box approach	**Proposed formulation**
Freshwater consumption (kg)	469.2	691
Percentage freshwater reduction	57.5	37.4
Amount of regenerated water (kg)	649.5	199.7
Duration of regeneration (h)	3.4	2
Total energy consumption (Wh)	9.8	6.7
Percentage energy savings	-	31.6
Wastewater storage size (kg)	383.964	222.6
Diluate storage size (kg)	310	189.8
Total cost of water network (c.u./y)	105425.8	91360.7
Percentage savings in network cost		13.3

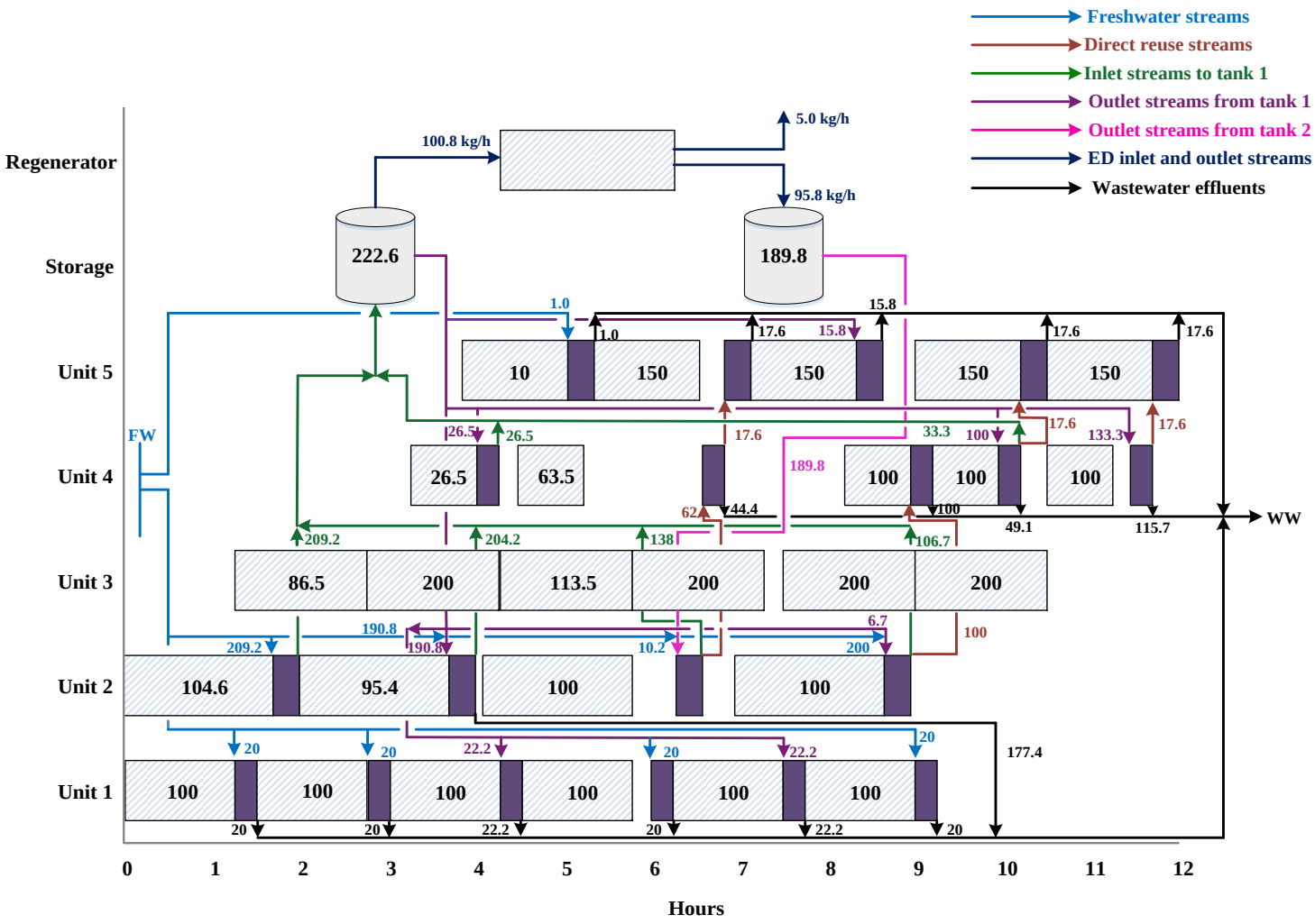
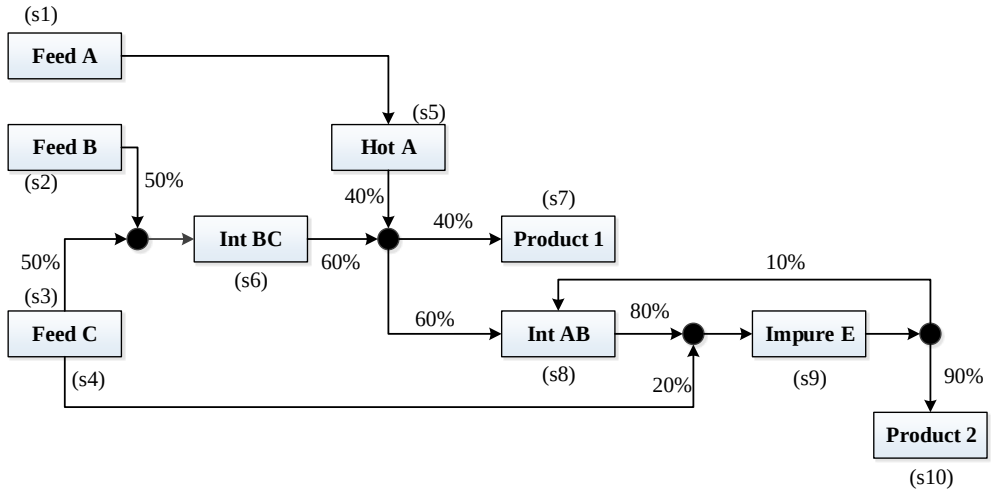


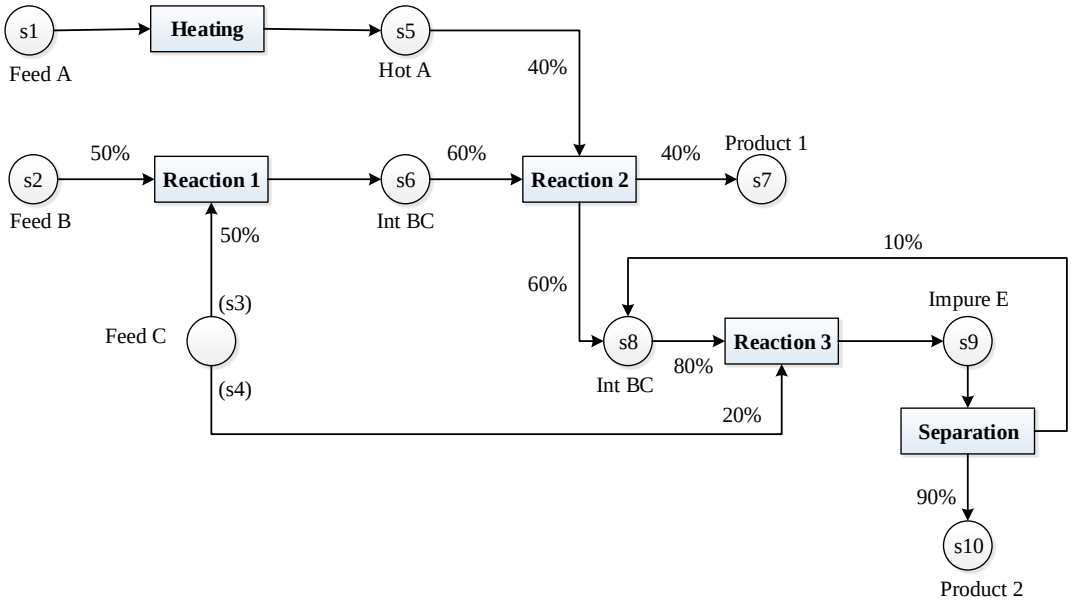
Figure 4.2 *Gantt chart for case study I*

4.3 Case study II

The second example is adapted from Kondili et al. (1993) who first presented the case study for the validation of their scheduling model, and Halim and Srinivasan (2011) who included additional data required for water integration. The case study consists of a multipurpose batch plant which aims to manufacture two products using three different raw materials. The production recipe involves a preheating process, three reactions occurring in two reactors and a separation process. Figure 4.3 gives the STN and SSN representation of the recipe to be followed for the manufacturing of products 1 and 2. It also shows, for each task, the percentage of feed required and percentage of intermediate and final products to be produced. Table 4.8 and Table 4.9 contain input parameters essential for the scheduling of the plant. It is worth mentioning that this case study considers the processing time of a task to be dependent on its batch size. Table 4.10 gives a set of parameters pertaining to washing operations for units with cleaning requirements with magnesium chloride ($MgCl_2$) being the contaminant to be removed. From Table 4.10, it can be seen that washing operations are only required for the two multipurpose reactors to avoid contamination between the three different reactions occurring in these units.



(a) SSN representation



(b) STN representation

Figure 4.3 *SSN and STN representation for production recipe of case study II*

Table 4.8 *Production scheduling data for case study II*

Units	Suitability	Capacity	Fixed processing time (h)	Variable processing time (h)	Washing time (h)
Heater	Heating	100	0.667	0.007	0.00
Reactor 1	Reaction 1	50	1.334	0.027	0.25
	Reaction 2	50	1.334	0.027	0.25
	Reaction 3	50	0.667	0.013	0.25
Reactor 2	Reaction 1	80	1.334	0.017	0.30
	Reaction 2	80	1.334	0.017	0.30
	Reaction 3	80	0.667	0.008	0.30
Still	Separation	200	1.334	0.007	0.00

4.3.1 Results and discussions

Table 4.11 gives the computational results for case study II and compares them with results obtained from the case where no process integration was employed. For this case study, the proposed formulation was able to reduce freshwater intake by 41.1% while maintaining the same production revenue. It is worth mentioning that the base case, i.e. the formulation with no integration, does not cater for additional costs of the water network such as regeneration and storage costs. Hence, no comparison was performed between the two cases in terms of the annualized plant profit as shown in Table 4.11. Table 4.11 also gives the model statistics for both cases and, similar to the first case study, the proposed formulation yielded a higher CPU time.

Table 4.9 *Additional scheduling data for case study II*

Material state	Initial inventory	Max storage (kg)	Revenue or cost (c.u/kg)
Feed A	1000	1000	10
Feed B	1000	1000	10
Feed C	1000	1000	10
Hot A	0	100	0
Int AB	0	200	0
Int BC	0	150	0
Impure E	0	200	0
Product 1	0	1000	20
Product 2	0	1000	20
Freshwater	-	-	0.1
Wastewater	-	-	0.05

Table 4.10 *Process integration data for tasks requiring washing for case study II*

Units	Task	Max inlet concentra-tion (ppm)	Max outlet concentration (ppm)	Contaminant loading (g $MgCl_2$/kg batch)
Heater	Heating	-	-	-
Reactor 1	Reaction 1	500	1,000	0.2
	Reaction 2	10	200	0.2
	Reaction 3	150	300	0.2
Reactor 2	Reaction 1	50	100	0.2
	Reaction 2	30	75	0.2
	Reaction 3	300	2,000	0.2
Still	Separation	-	-	0.2

The Gantt chart obtained as a result of the implementation of the proposed formulation for this case study is shown in Figure 4.4 It gives the sequence of tasks and network configuration the plant has to follow in order to achieve the optimum plant profit given in Table 4.11. The model yielded a water network with opportunities for freshwater use, indirect and regeneration reuse whilst no direct reuse opportunities where found. The regenerator operated for 2.6h with the process starting at time 5.9h within the time horizon. The delay in the starting time of the regeneration process is explained by the fact that the wastewater storage tank needed to have a considerable amount of water to allow the ED regenerator to operate continuously. The short operation time of the regenerator is due to the fact that this formulation forces both the diluate and wastewater storages to be empty at the end of the time horizon of interest. In a cyclic scheduling problem, this constraint could be relaxed to allow for reuse between different production cycles within the facility. The design specifications of the ED regenerator required for this plant are given in Table 4.12. The regenerator is ED stack of 0.7 m length which contains 10 cell pairs and requires a total membrane area of 5.9 m^2. The energy requirements, flow velocity and process efficiency of the electrodialysis regenerator are also included in Table 4.12.

Table 4.11 *Detailed results for case study II*

	No integration	**Proposed formulation**
Annual Profit (c.u×10^5)	-	31
Freshwater (kg)	735.0	430.4
Revenue (c.u) for 12h horizon	4665.3	4665.3
Percentage freshwater saving	-	41.4
No. constraints	1,548	3,798
No. variables	794	1,420
No. discrete variables	104	325
No. binary variables	104	225
Non-linear terms	84	848
CPU time (s)	1.49	28,000

Table 4.12 *Design specifications for the ED unit in case study II*

Design variables	**Optimum values**
Membrane area(m^2)	5.9
No. cell pairs	10
ED stack length(m)	0.7
Desalination energy (kWh/y)	1.101
Pumping energy (kWh/y)	0.096
Electric current (A)	0.400
Product recovery rate	0.95
Linear velocity(m/s)	0.013

The advantages of adopting the proposed mathematical formulation over a black-box approach are demonstrated in Table 4.13. It compares the water network

specifications obtained using the proposed formulation with those obtained using the black-box approach described in Section 4.2.1. It can be seen that both approaches gave the same freshwater consumption whilst an increase in the amount of regenerated water was observed in the black-box approach. As a result, the size of storage tanks and the amount of energy consumed increased, resulting in a higher cost of the water network. The proposed formulation achieved the same water consumption by favouring the exploration of direct and indirect reuse which came at a lower cost compared to feeding the regenerator with more wastewater as suggested by the black-box approach. Therefore, a 0.56 % and 9.87 % decrease in water network cost and energy consumption respectively was achieved by the proposed optimization approach. This demonstrates the importance of designing a regeneration operation with enough details to enable the objective function of an optimization problem to capture its accurate cost.

Table 4.13 *Comparative results from black-box and detailed modelling approaches*

	Blackbox approach	**Proposed formulation**
Freshwater consumption (kg)	430.4	430.4
Amount of regenerated water (kg)	289	259.4
Duration of regeneration (h)	1.4	2.6
Total energy consumption (Wh)	3.5	3.1
Percentage energy savings	-	9.87
Wastewater storage size (kg)	369.6	259.7
Diluate storage size (kg)	274.6	246
Total cost of water network (c.u./y)	66257	65884.3
Percentage savings in network cost	-	0.56

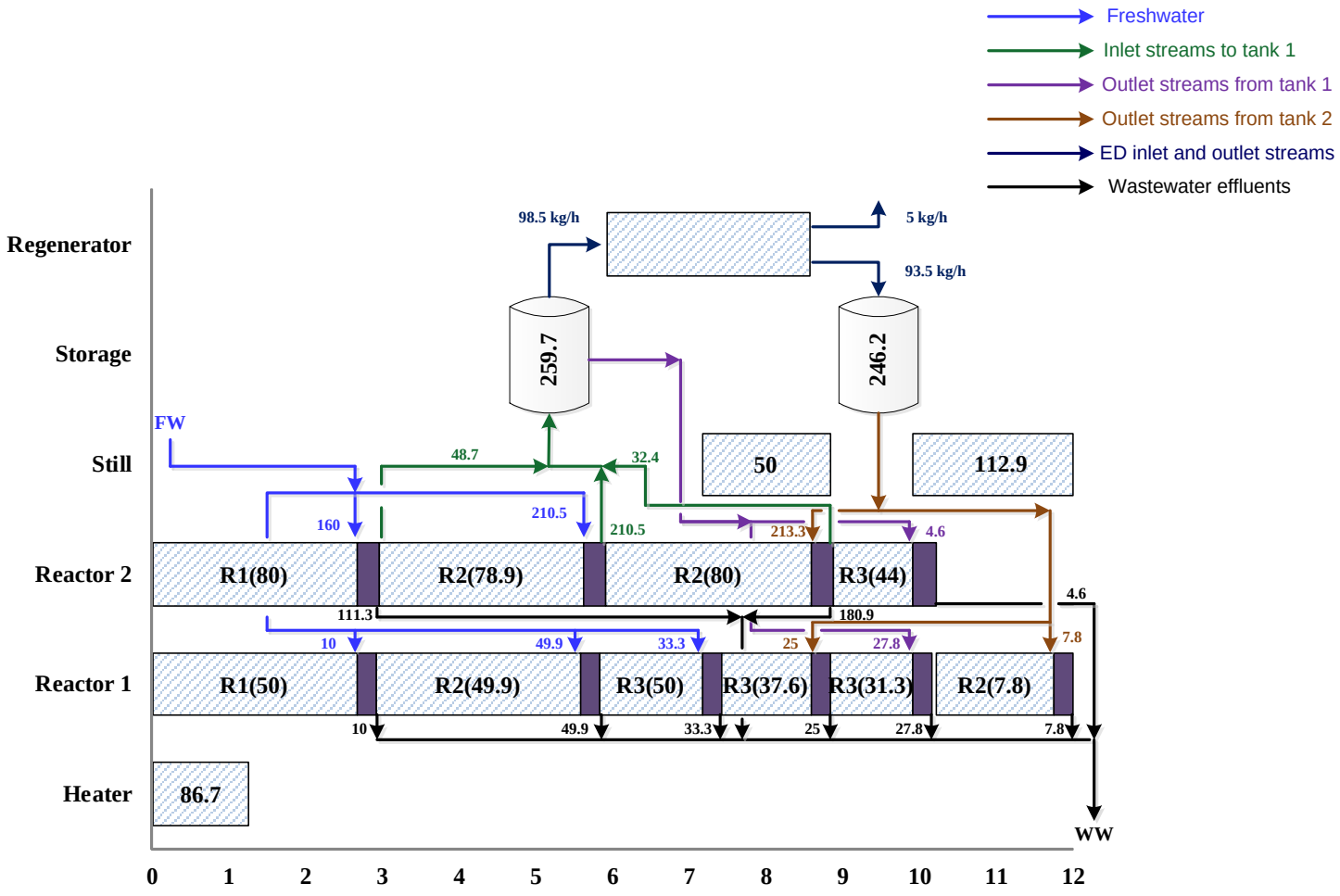


Figure 4.4 *Gantt chart for case study II*

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5

INDUSTRIAL CASE STUDY

5.1 Introduction

Dairy processing plants require a considerable amount of water to maintain standard levels of cleanliness and hygiene and avoid any growth of pathogenic microorganisms which can cause serious health hazards. A case study on the reduction of water consumption was undertaken at Amul processing plant, one of the biggest producers of dairy products in both India and the world. Raw milk is collected from approximately 700 thousand villagers and processes 1800 cubic meter of milk per day while the daily water requirement is currently set at 1600 cubic meters (Buabeng-Baidoo, et al., 2017). Their main products are milk, ghee, butter, flavoured milk and milk powder. The plant is accordingly divided into the raw milk receiving department (RMRD), powder, ghee, flavoured milk, skimmed milk powder and milk packaging sections as shown in Figure 5.1. The total annual consumption of water in this plant is currently at six millions of cubic meter per annum. 75% of the total water consumed is used in cleaning in place (CIP) and floor cleaning processes while the remaining 25% is directed to other operational duties as shown in Figure 5.2. These duties include the usage of water for cooling tower make up, boiler feed make up, operational processes, railway tanker wash, and many other processes.

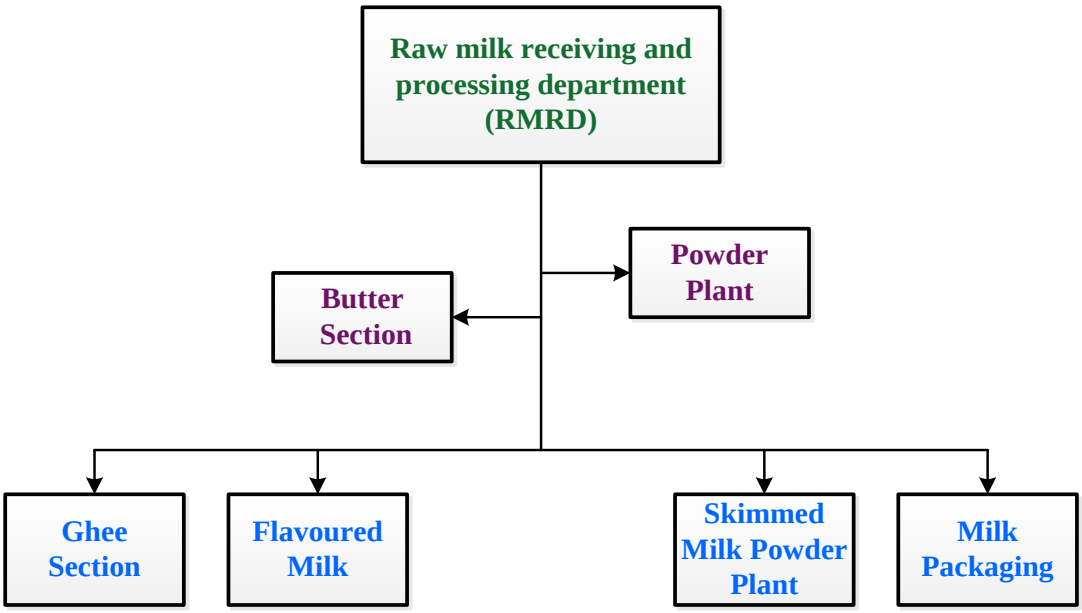


Figure 5.1 *Amul dairy production plant scheme*

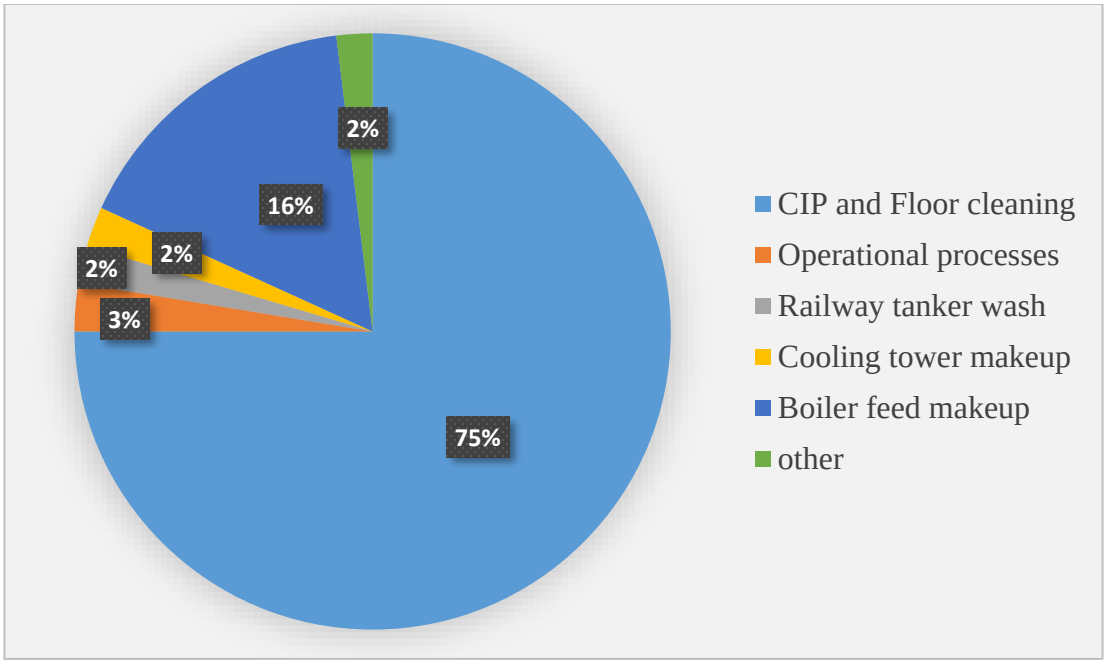


Figure 5.2 *Distribution of water consumption in Amul dairy plant*

CIP is an automated cleaning procedure of various processing units, pipes, tanks and other facilities to maintain the required hygiene standards. It involves the use of

controlled valves and pumps to achieve programmed water flow and circulation when required. Traditional cleaning in the dairy industry was performed by plant operators who used to disassemble the equipment to be cleaned, enter the vessel and clean the affected areas. The hygiene standards of the plant were rarely met due to the inaccuracy associated with human errors. CIP then arose to most importantly ensure the safety of workers by reducing manual cleaning operations. It also has the advantage of achieving high sanitation qualities by reducing human errors through automation hence allowing the controlled use of water, energy and other resources involved in cleaning procedures (Memisi, et al., 2015). At Amul, CIP is mainly required in the RMRD, butter, ghee, flavoured milk and milk packaging sections of the plant. The RMRD plant consumes 89 % of the total amount of water directed to the CIP operations as shown in Figure 5.3. This implies that reducing water consumption in this section of the plant will result in considerable water saving in the entire plant. Therefore, it is essential to explore process integration opportunities for the minimization freshwater use in the RMRD of Amul.

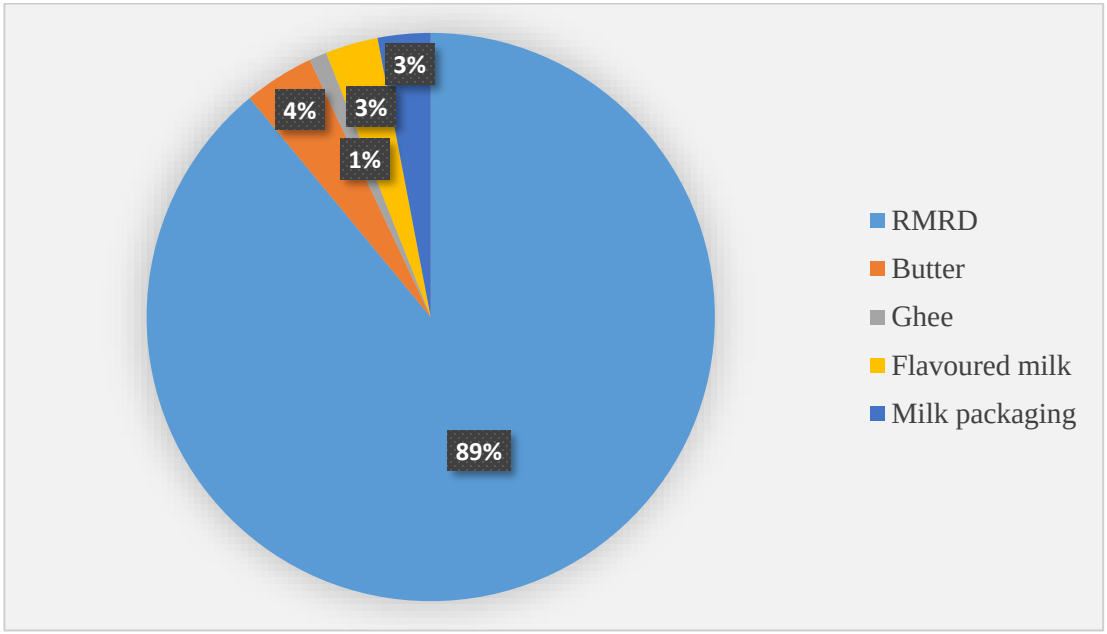


Figure 5.3 *Water use distribution in the CIP and floor cleaning sector of Amul dairy plant*

5.2 RMRD process description

The RMRD plant aims to convert raw milk into marketable milk that can either be further processed in other section of the plant to produce diverse dairy products or sent to the milk packaging section to be delivered to consumers. Figure 5.6 gives the process flow diagram of the RMRD with all equipment and operations involved. The process starts with raw milk being transported from the collection point to the plant using a road tanker at a temperature of around 7 to 10˚C. The milk undergoes filtration to remove any present foreign body that may be present in the milk. The filtered milk is then pumped to a chiller where its temperature is reduced to around 3 to 4 ˚C and stored in a buffer tank. The cold milk is then pumped from the buffer tank into the clarifier to remove the remaining impurities such as fine particles with may have escaped removal in the filtration process. The sludge from the clarification process is sent to a sludge collector tank while the clarified milk is stored in the raw milk silos.

From the clarification process, milk goes through a circuit involving milk separation, standardization, and pasteurization. The cold milk from the silos is pumped into a regenerative heat exchanger, also referred to as pasteurizer, where its temperature is increased to around 40 to 50 ˚C. The regenerator is a special type of heat exchanger which allows for the intermittent exchange of heat between hot and cold fluids by using a heat transfer medium for temporary storage of heat (Willmott, 2011). The hot milk then passes through a conventional heat exchanger where the temperature is raised to about 50 to 60 ˚C and enters the separation process. The milk is separated into skim and cream which are temporarily stored and maintained at a temperature of 62 ˚C. The standardization of milk then takes place whereby the skim is gradually mixed with a portion of cream to achieve the desired fat content and the remaining cream is transferred to other plant sections where cream pasteurization takes place. The milk produced from the standardization enters the pasteurization process where it passes through another heat exchanger set comprising of a regenerator and a heat exchanger. It then exits at a temperature of 78 ˚C and stored in an insulated holding

tank for a certain period of time. The purpose of pasteurization is to increase milk shelf life and safety by destroying pathogens and spoilage microorganisms and enzymes (Chandan, et al., 2016).

Hot milk is then pumped from the holding tank to the first regenerator where it undergoes rapid cooling by exchanging heat with the cold medium hence reducing its temperature from 78 ˚C to 10 ˚C. It is further cooled by passing through the chiller and exiting at a temperature ranging from 3 ˚C to 4 ˚C. Milk homogenization then occurs by pumping cold milk through a set of orifice valves. The purpose of homogenization is to break down fat molecules contained in the milk in order to prevent them from forming a cream layer at the top of the bulk (Tomasula, et al., 2013). The product of the homogenization process is sent to the milk storage or packaging section for a later delivery to consumers.

5.3 Flowsheet simplification and CIP in the RMRD

CIP of facilities in the RMRD is regularly performed after each processing cycle. The main units in which intensive cleaning is carried out are pasteurizers, tanks, separators, and pipes. For modelling purposes, the plant flowsheet shown in Figure 5.6 is simplified into the block flow diagram shown in Figure 5.4 by grouping processing units into main processing stages. The resultant STN representation is then given in Figure 5.5. The proportion of clarified milk and slugde production produced from clarification process is respectively given as 98 % and 2% of the amount of milk entering the clarification stage. Similarly, the heating and separation process produce an equal amount of skim and cream while the separation process requires 80 to 20 % skim to cream ratio of as shown in Figure 5.4. It is worth pointing out that the ratio of skim to cream fed into the standardization process depends on the desired fat content required in the final product and this may vary from one production cycle to the other. However, for the purpose of this work the recipe of milk production was fixed hence the aforementioned ratio was adopted for the time horizon of interest.

The input data pertaining to the scheduling of the RMRD section are given in Table 5.1. This includes the duration of each processing stage, the maximum amount of milk that can be processed at each stage and the time it takes to complete washing operations. The quantity of raw milk processed daily was set at 1.2 million per day. A time horizon of 24 hours was considered while UIS was applied to all intermediate materials. This was done to ensure that the abovementioned quantity milk to be processed daily is entirely consumed by the process.

Table 5.2 comprises of the inputs parameters necessary to perform water integration between various units requiring washing. It is worth noting that more than one equipment unit require washing after each processing stage. Hence the amount of water required per stage was given as the total amount of water resulting from the sum of water quantity required by each unit. In a similar fashion, the load of contaminants to be removed at each stage was obtained. The limiting concentrations of the inlet and outlet water streams to and from each washing operation are also given in Table 5.2.

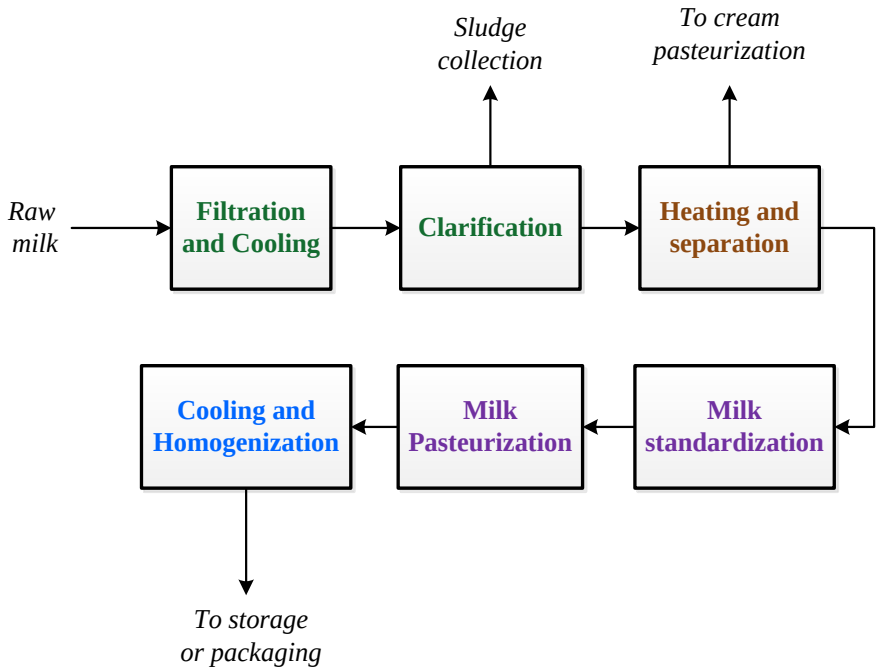


Figure 5.4 *Simplified block flow diagram for the RMRD*

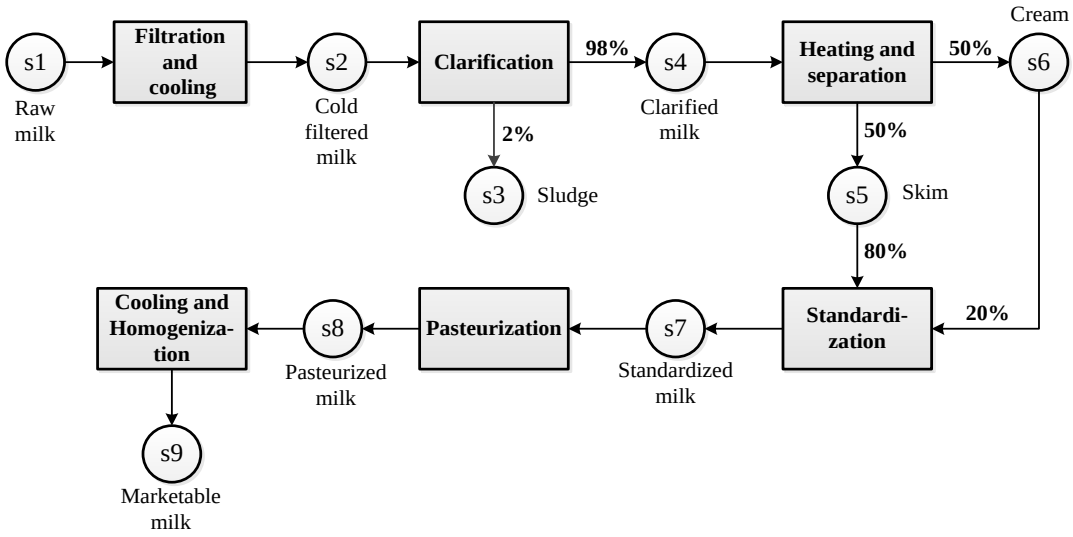


Figure 5.5 *STN representation of the RMRD production recipe*

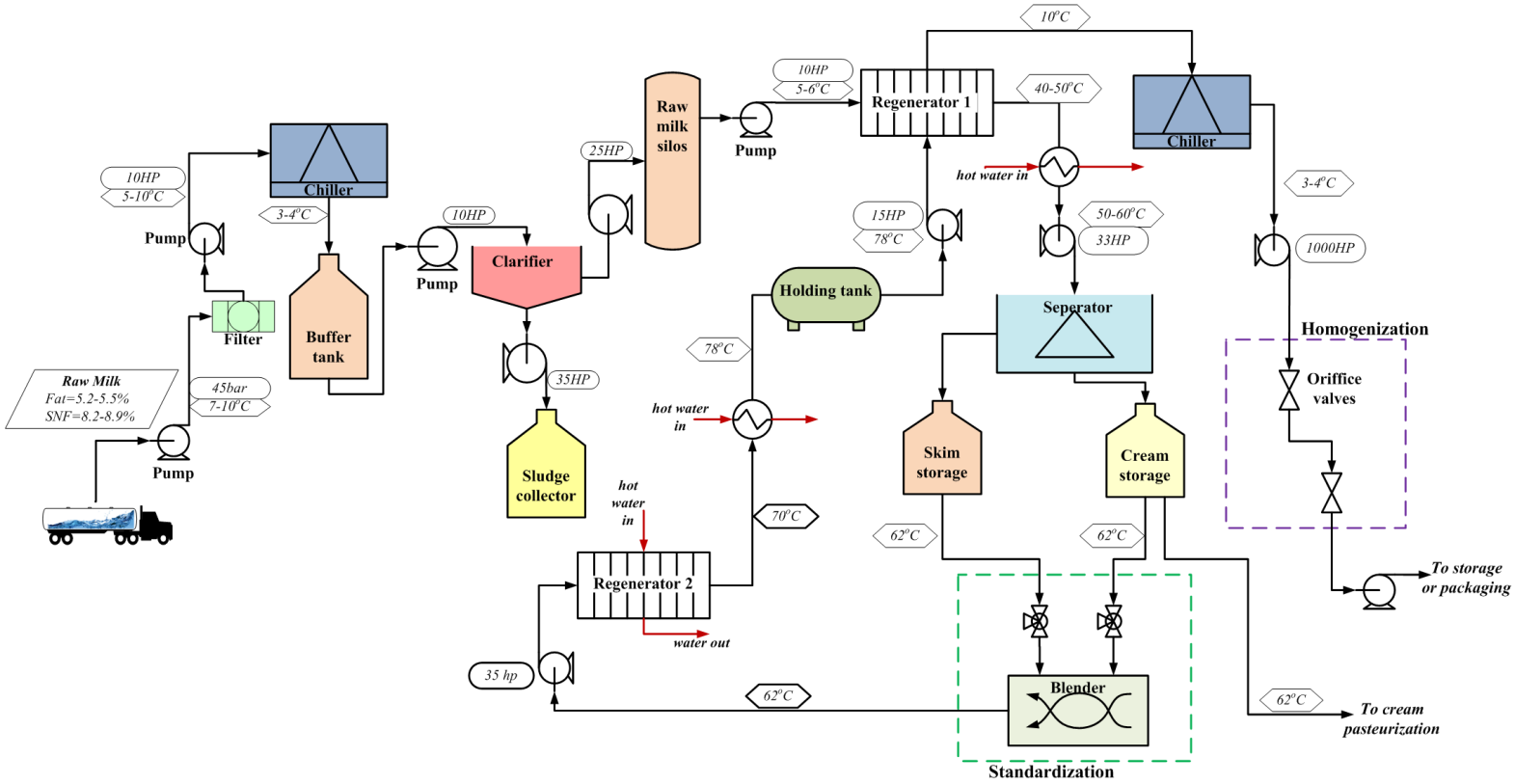


Figure 5.6 *Process flow diagram in the RMRD*

Table 5.1 *Scheduling data for the milk receiving plant at Amul dairy*

Process stages	**Duration (h)**	**Batch size (tons)**	**Washing requirements**	**Duration (min)**
Filtration and cooling	2	450	Pipes	20
Clarification	3	450	Buffer tank, pipes	30
Heating and separation	3	450	Raw milk silos, separators, pipes	30
Standardization	3	450	Skim and cream storage tanks, pipes	20
Pasteurization	2	450	Pasteurizer and pipes	30
Cooling and homogenization	3	450	Holding tank, pasteurizer, and pipes	35

Table 5.2 *Limiting data for water integration*

Process stages	**Water requirement (tons)**	**Mass load (kg TDS)**	**Max Inlet Conc. (kg TDS/tons)**	**Max Outlet Conc. (kgTDS/tons)**
Filtration and cooling	12.4	0.62	0.02	0.07
Clarification	22.8	0.99	0.05	0.09
Heating and separation	37.3	1.64	0.04	0.08
Standardization	35.2	1.47	0.05	0.09
Pasteurization	26.9	1.29	0.07	0.12
Cooling and homogenization	42.2	1.98	0.05	0.09

The schedule of the plant prior to applying the proposed formulation is given in Figure 5.7. The figure shows that each processing stage comprised of a sequence of 3 batch tasks and 3 washing operations. Freshwater is used as the only water source in the plant while wastewater generated from each washing task is directly discharged as effluent. It is worth pointing out that the amount of freshwater used by each washing operation is maintained at a fixed value for each unit as per operational specifications. A total of 530.4 tons of water is used per day in the RMRD department. The daily amount of raw milk processed, milk and cream produced are maintained at 1239.6, 759.3 and 455.6 tons respectively.

5.4 Optimization of the RMRD water network

A recent work presented by Buabeng-Baidoo et al. (2017) was performed in the RMRD of Amul to integrate its water network and minimize its freshwater consumption. A network of reverse osmosis regenerators was used to facilitate regeneration reuse within the plant. The outcome of their work suggested that a considerable reduction of freshwater intake could be achieved through the direct reuse of both wastewater and treated water. However, their approach was adapted from a superstructure optimization model developed for continuous processes. The results obtained from their technique could therefore not be implemented in the plant due to the fact that the schedule of the plant was not considered in the problem formulation.

The mathematical model presented in Chapter 3 was then applied to the Amul RMRD in order to minimize freshwater consumption using an optimization approach suitable for batch processes. Similar to the Illustrative examples presented in Chapter 4, the solution to the optimization of the Amul plant was obtained by formulating the MINLP model in GAMS 24.3.3 and using BARON. The processor used to implement models in the previous chapter was used for this case study. As shown in Table 5.3, the proposed formulation optimized the water network of the Amul dairy by reducing the freshwater consumption of the RMRD by 22 %. The production requirements

were maintained as specified in the base case scenario where no integration is performed on the water network.

Table 5.3 *Computational results for industrial case study*

	No integration	**Proposed formulation**
Raw milk processed (tons)	1239.6	1239.6
Milk produced (tons)	759.3	759.3
Cream produced (tons)	455.6	455.6
Freshwater consumption (tons)	530.4	331.6
Wastewater generation(tons)	530.4	331.6
Percentage freshwater saving	-	37.5

The formulation of the optimization problem for the minimization of the water usage in the RMRD of Amul yielded a MINLP model with statistics given in Table 5.4. The scheduling standalone model without water integration provided a solution in a very small CPU time of 0.14 seconds while the addition of reuse constraints and ED design constraints increased the computational time to 28,790 seconds. The computational expensiveness of the proposed formulation was elaborated in Chapter 4. A similar behaviour was observed in this case whereby a drastic increase in number of constraints, continuous and discrete variables, as well as the number of nonlinear terms, was caused by the exploration of water reuse opportunities in the plant This again resulted in a very high CPU time as opposed to the case where the plant schedule alone was optimized, i.e. the case with no integration

Table 5.4 *Model statistics*

	No integration	**Proposed formulation**
No. constraints	925	6,902
No. continuous variables	601	1,785
No. discrete variables	48	491
No. binary variables	48	391
Non-linear terms	96	1,202
CPU time (s)	0.14	28,790

Table 5.5 gives the dimensions of the ED stack required by the plant to allow regeneration reuse. An ED stack of 0.7 m long with a total membrane area of 17.2 m^2 arranged into 30 compartments or cell pairs was obtained. 851.8 kWh per annum of energy will be directed towards desalting of wastewater streams while 18.5 kWh of energy per annum will be consumed to feed wastewater into the ED Stack. The required electric current, liquid recovery ratio and linear velocity of the wastewater streams are specified as 3.088 A, 0.95 and 0.055 m/s as given in Table 5.5.

Table 5.5 *Design specifications for the ED regeneration process*

Design variables	**Optimum values**
Membrane area(m^2)	17.6
No. cell pairs	30
ED stack length(m)	0.7
Desalination energy (kWh/y)	851.8
Pumping energy (kWh/y)	18.5
Electric current (A)	3.088
Product recovery ratio	0.95
Linear velocity(m/s)	0.055

The proposed configuration of the RMRD of Amul dairy is illustrated in Figure 5.8. The Gantt chart shows the number of batches and washing operations performed at each processing stage. It also specifies the size of each batch and shows all water streams entering and leaving washing operations. For instance, 3 batches of 340, 450 and 450 tons each are processed in the filtration and cooling stage. It can also be seen that consecutive batches are separated by washing operations. The first washing operation after the completion of the first batch receives 12.4 tons of freshwater and transfers the same amount of water to storage once it is completed. The second washing operation receives 3.6 tons of water from storage and dilutes it with 8.9 tons of freshwater. At the end of the second washing operation, 8.9 tons of freshwater is directly reused in the first washing operation of the clarification stage and 3.6 kg is directly discharged as wastewater effluent from RMRD. Similar to the first washing operation in the clarification process, the third operation receives 12.4 tons of freshwater at the beginning of its operation and transfers the entire amount to storage once it reaches completion. It is worth mentioning that in this formulation, the quantity of freshwater required in each washing operation was fixed to the value given in Table 5.2 as specified in the plant. The processing batches and washing tasks in the remaining stages can be interpreted similarly. The wastewater and diluate storage tanks were both designed, and their optimum capacity was obtained as 12.4 and 18.7 tons respectively as shown in Figure 5.8. The regenerator is intended to operate for 15.2 hours at a feed rate of 1.3 tons per hour. This allows a total of 19.8 tons of wastewater to be purified at a removal ratio of 90 % and a liquid recovery ratio of 95% as given in Table 5.5.

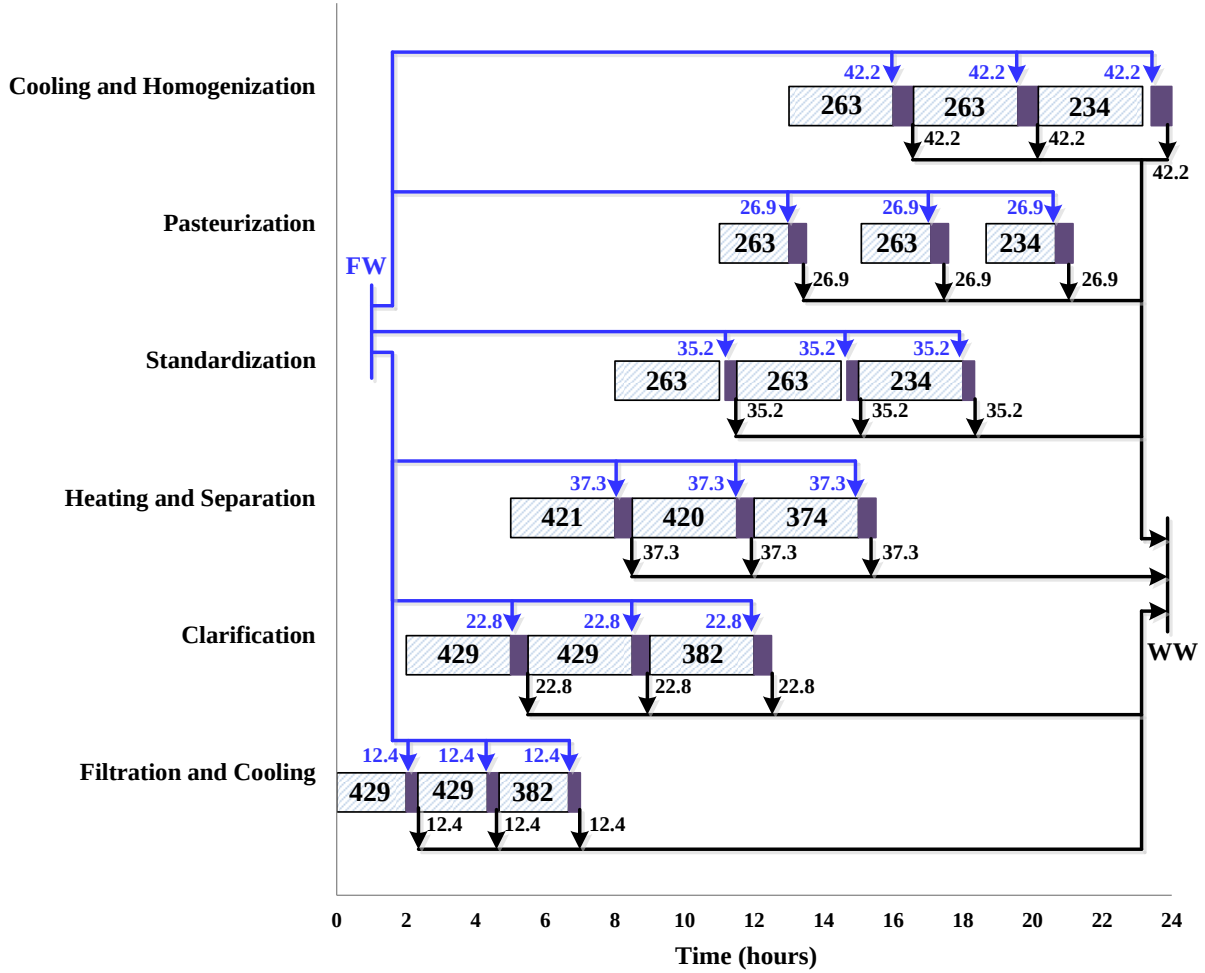


Figure 5.7 *RMRD plant schedule prior to water integration*

A modification in the schedule of the RMRD is observed when comparing Figure 5.7 and Figure 5.8. The number of batches processed in the standardization, pasteurization, and the cooling and homogenization stages was reduced from three to two batches. The milk production was conserved by increasing the batch size while still satisfying the maximum capacity constraint of 450 tons per batch. This then reduced the number of washing operations required hence resulting in a decrease in freshwater intake. The advantage of a flexible scheduling technique is also shown when comparing both plant schedules. The start and end time of washing operations were modified to find more water reuse opportunities in the plant as shown in Figure 5.8. However, it is worth mentioning that more batches could be fit in the first 5 processing stages to maximize the production of milk in the next 24 hours. This could suppress some reuse opportunities around washing operations due to the restrictions on the flexibility of the schedule. Therefore, the plant schedule proposed in Figure 5.8 can be used as a guideline for the plant to reduce its freshwater intake.

Table 5.6 gives the main components contributing to the cost of the integrated water network and their economic value in the proposed plant setup. The unit cost of freshwater, wastewater and, electricity was specified as 1 c.u per ton and 0.06 c.u. per kWh respectively (Buabeng-Baidoo, et al., 2017). The capital cost of ED and storage were calculated using the cost data specified in Table 4.4. Prior to applying the formulation, the freshwater cost and wastewater disposal cost were the main contributors to the total water network cost. The implementation of the proposed technique added some additional aspect to the water network costs, i.e. capital cost of ED and storage tanks and the electricity cost associated the energy consumption of the regeneration process. The economic analysis shows that the reduction in freshwater intake outweighed the additional costs associated with the exploration of water reuse opportunities. Hence a total reduction of 20.2 % in operating costs was achieved by implementing the proposed technique. Unlike the costs of water and energy consumption, the capital costs are not recurring. However, as formulated in the objective function described by Constraint (3.99), the capital costs of ED and

storage were annualized based on the equipment life which was estimated to be 5 years in this case. The revenue was not included in the costing calculations as this will remain constant since the amount of milk and cream produced remained unchanged after implementing the proposed technique. This then entails an increase in the overall profit of the plant.

Table 5.6 *Cost-benefit analysis of the proposed plant configuration*

	Current plant	**Proposed plant setup**
Annual freshwater cost	150150	109420
Annual wastewater cost	150150	109230
Annualized ED capital cost	-	528
Annualized cost of storage	-	20578.2
Electricity cost	-	2609.6
Total annualized cost	300300	239670.6
Percentage saving in water network cost		19.2

The computational results obtained from the proposed optimization approach were compared to the results of obtained from a typical black-box approach as described in Chapter 4. Table 5.7 gives the design specifications of the water network obtained from both approaches. The black-box approach was able to achieve a higher reduction in freshwater consumption from the initial amount of 530.4 tons compared to the proposed formulation. The increase in freshwater reduction was made possible by feeding a greater amount of wastewater in the regenerator at a higher flowrate. This explains the short duration of the regeneration process compared to the proposed setup. The energy consumption amounted to 55.2 Wh as opposed to 2.6 Wh of energy requirement in the proposed plant setup. Furthermore, the black-box approach

suggested a water network setup with storage capacities of 44.5 tons and 42.2 tons each compared the capacities of 12.4 and 18.7 proposed by the developed technique. Therefore the adoption of the proposed formulation over the black-box approach yielded 95.2 and 10.8 decrease in energy consumption and total water network cost respectively.

Table 5.7 *Comparative study between black-box and detailed modelling approach*

	Black-box approach	**Proposed formulation**
Freshwater consumption (tons)	294.6	331.6
Amount of regenerated water (tons)	44.5	20.3
Duration of regeneration (h)	7.8	15.6
Total energy consumption (Wh)	55.2	2.6
Percentage energy savings	-	95.2
Wastewater storage size (tons)	44.5	12.4
Diluate storage size (tons)	42.2	18.7
Total cost of water network (c.u./y)	272054	242572
Percentage savings in network cost		10.8

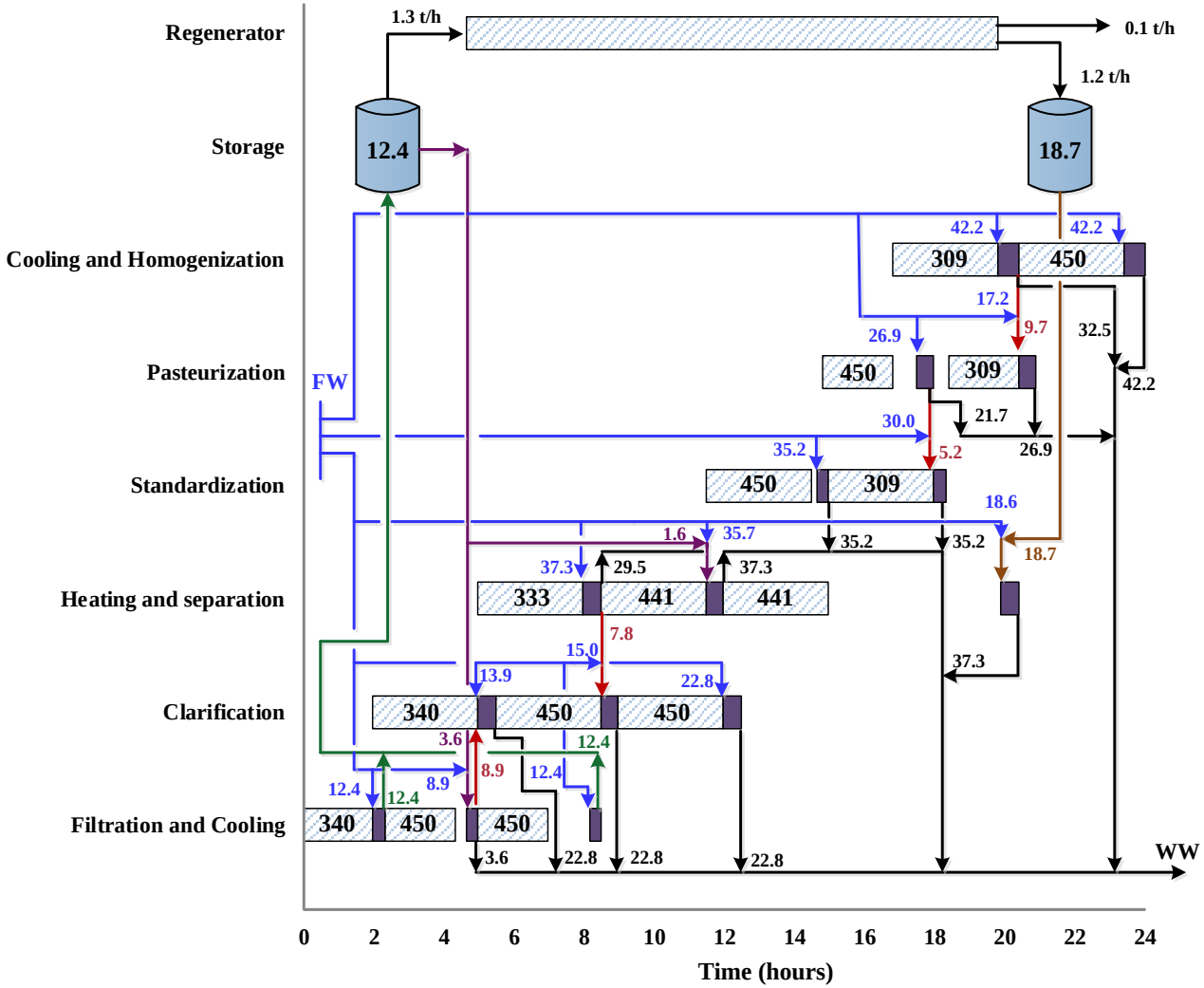


Figure 5.8 *Gantt chart representing the proposed schedule and water network of Amul RMRD.*

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6

LIMITATIONS AND RECOMMENDATIONS

6.1 Introduction

The wastewater minimization technique developed in this work was verified and validated against two illustrative examples. Its practicality was also tested by applying it to a real industrial process. Several challenges were encountered during its implementation due to the omission of some important practical considerations. Furthermore, the structure and nature of the model influenced the computational challenges faced as mentioned in previous chapters. This chapter highlights and discusses the main limiting aspects of the proposed formulation and elaborates on possible avenues of future improvement.

6.2 Water network limitations

6.2.1 Single contaminant

The proposed formulation was developed for wastewater minimization problems with a single key contaminant. This entails that all existing water streams were characterized by one common contaminant. This assumption has proven to reduce the complexity of the resultant model at the expense of reducing its practicability in the

process industry. Wastewater streams with multiple contaminants are more prevalent to industrial water networks as compared to single contaminant. This is many due to the fact that tasks involved in a typical batch production scheme are inherently different. Therefore, it is of utmost importance for this work to be adapted to multiple contaminant problems for a possible increase in its industrial applications.

6.2.2 Water-using operations

The batch water network was optimized in this work by exploring reuse opportunities between various washing operations. Washing operations are typical examples of mass transfer processes. A mass transfer operation entails the transfer of contaminants from a rich stream, i.e. a stream with higher contaminant concentration, to a lean stream, i.e. a stream with lower contaminant concentration. In the case of washing operations, processes are considered as rich streams and water streams used to clean these processes are lean streams. Another example of a mass transfer-based mechanism is the solvent extraction process. However, there can be instances where a process itself produces water as a by-product or consumes water as a feedstock or reactant. These types of processes are called non-mass transfer processes and cannot be modelled using Constraints (3.3) and (3.5) as presented in Chapter 3. In the event where non-mass transfer processes are large contributors to the freshwater consumption or wastewater generation of a batch process, the abovementioned constraints will be omitted in their mathematical representation. Constraint (3.1) and (3.2) will then be used interchangeably depending on the type of non-mass transfer process involved in the water network.

6.2.3 Water treatment technology

The quality of industrial wastewater effluents is usually measured by their physical, chemical and biological composition. The major constituents of concern in wastewater treatment for reuse or disposal are the suspended solids, dissolved inorganics, heavy metals, nutrients, pathogens, biodegradable and refractory organics

(Tchobanoglous, et al., 2003). Several indices are used as collective measures of those components and this includes the Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), etc. The water network embedded an electrodialysis (ED) treatment unit to partially purify wastewater effluents and facilitate their reuse within the process. The advantage of ED relies on its ability to efficiently purify effluents without requiring intense pre-treatment, relatively easy cleaning procedure and can even be self-cleaned through electrodialysis Reversal (EDR) (Chao & Liang, 2008). It is also suitable for intermittent systems such as batch systems due to its relatively simple start up and shut down procedure (Strathmann, 2004).However, ED is limited to the removal of ionic compounds in wastewater. This then suppresses its applicability to a typical industrial water network with multiple contaminants.

The extension of this formulation to a wider range and variety of contaminants will require an enhancement of the wastewater system. This entails adapting the formulation to multi-contaminants water systems by having a network of wastewater treatment technologies in the problem superstructure. For Instance, in the industrial case study presented in Chapter 5, the quality of wastewater effluents was measured by their concentration in total dissolved solids (TDS) to facilitate the treatment though ED. However, wastewater from dairy processes contains various other contaminants such as TSS and biodegradable organics measured by the COD or BOD. The network could consist of a combination of many other technologies such as Reverse Osmosis (RO), Nanofiltration (NF) and Ultrafiltration (UF) which can be configured in series or parallel. Since each technology has its own contaminant selectivity, this would allow the model to then select the type of technology suitable for the treatment of effluents generated within a given batch water network

In this formulation, a preliminary design of the ED process was performed to mainly determine the size of the stack, the total membrane area required and the total consumption of energy. The contaminant removal rate of the ED process was defined

as a parameter during optimization. Future work should enhance the ED design by providing more details with regards to the type and properties of membranes and design of spacers. Spacers are placed between membranes to ensure uniform flow in each ED cell, maximize mixing of solutions at the surface of membranes and minimize pressure loss. The type of spacers is also a key determiner of the flow path through the ED stack (Strathmann, 2004). It is also advisable to explore the case where the contaminant removal rate is determined through optimization. However, this could drastically increase the CPU time hence alternative optimization routes will be discussed later in this chapter.

6.3 Scheduling considerations

The schedule of a batch plant is a key aspect in the optimization of its water network. The discrete occurrence of water using operations within a given production scheme showed the importance of an adequate plant scheduling. This has allowed for more water reuse opportunities to be obtained since the optimization of the plant schedule and batch water network were performed simultaneously as mentioned in Chapter 4 and 5. The scheduling model adopted in this work was mainly formulated for multipurpose batch plants. The main scheduling decisions that were made were the allocation of tasks to units, batch sizing, and sequencing decisions. However, in practice, the level of decision making in production scheduling may vary from one plant to the other depending on the decisions made by the higher management. This is mainly due to the fact that the scheduling task forms an integral part of a supply chain management and interactions between various functions is plant specific. For instance, if the decision of batch sizing is made at the planning level, then scheduling will be reduced to only assigning tasks to units and determining the optimum sequences of tasks (Harjunkoski, et al., 2014). Therefore, the scheduling model adopted in this formulation should be adapted to the production environment of particular a plant for a successful implementation.

This formulation considered a short-term scheduling of batch processes. This implies that the makespan within which batch tasks occur is limited to few hours or days. In fact, the highest time horizon considered in the presented case study and illustrative examples was 24 hours. Since the presented results are primarily dependent on the length of the makespan, the short-term scheduling consideration is a major limitation of the presented work. A longer time horizon would have tremendous impact on the batch production schedule and the water network design. It could incur changes in the design specifications of the electrodialysis process, the resultant sizes of storage and the reuse opportunities found around batch operations.

In order for this formulation to be applicable to medium and long-term scheduling problems, additional scheduling aspects such as cyclic production and scheduling under uncertainties will have to be considered. The concept of cyclic scheduling involves the incorporation of short-term scheduling concepts in long time horizons. It considers the repetition of an optimum schedule obtained within a short time horizon when the problem is extended to longer horizons (Nonyane & Majozi, 2011). This will then result in many cycles of the same sequence of tasks and allow the reuse of water streams from one cycle to the other through the use of storage vessels. However, the assumption of constant production schedule from one cycle to the other might prove to be unrealistic in market demands characterized by frequent variation in product demand. In this case, rescheduling of tasks will be required when sudden changes occur in production requirements as specified through demand forecasting (Harjunkoski, et al., 2014).

6.4 Computational intensity

Table 4.5, 4.10 and 5.4 previously discussed in Chapter 4 and 5 gives data showing the computational intensity of the proposed formulation. The results for both illustrative examples and the industrial case study were obtained in a high computational time of approximately 8 hours. The Challenge with high CPU time

arises when for instance rescheduling of a given batch plant is performed on a regular basis for production improvement or water network optimization. In this case, mathematical models with high computational burden will not be attractive to the industry. However, it is worth mentioning that the presented formulation involves the design of equipment such as regenerator and storage tanks and constraints used to describe those units mainly contributed to the computational burden. In the event where a wastewater regeneration unit and storage tanks are readily available within the plant, the problem formulation will be drastically simplified and the CPU time will be reduced. At a design level, a large CPU time is less problematic since no operation is being undertaken and the focus is on providing an optimum design of the plant. Nevertheless, it is important to discuss possible ways to improve the computational time and some will be elaborated in this section.

6.4.1 CPU time improvement

The computational expensiveness of the proposed formulation is mainly due to its structure and size. The statistics of the resultant models for all examples, as presented in Tables 4.5, 4.10 and 5.4, show that the formulations yielded large scale models with the number of constraints and variables ranging from 5200 to 6900 and 1600 to 2280 respectively. The nonlinearity and nonconvexity of the proposed formulation are other key aspects contributing to computational difficulties. Methods of CPU time reduction which might prove to be effective include convexification and pre-processing techniques. The type of solver, on the other hand, can contribute to the increase in computational time depending on the structure of the model. Pre-processing techniques are other ways in which the solution time can be improved in future work. These aspects are discussed and examined below.

(a) Convexification techniques

The use of convexification techniques is among the possible ways in which the CPU time of a MINLP problem can be reduced. This includes the Glover transformation,

the McCormick (1976) and Lundell et al. (2013) reformulation techniques discussed in Section 2.2.4 of Chapter 2. It is worth mentioning that Glover transformation has been applied to the existing model to linearize the bilinear term $\tau^{re}(p)y^{re}(p)$ found in Constraint 3.80 which defines the duration of the regeneration process. The McCormick estimation could be used to relax all bilinear terms found in most water balance constraints. The solution to the relaxed formulation could then be used as starting point in the exact MINLP problem. However, in the event where upper and lower bounds of variables are unknown or too large, this approach could result in an increase in CPU time due to the enlargement of the search space. The convexification techniques applied to the SGO algorithm of Lundell et al. (2013) can be also be used to reformulate bilinear terms and other signomial functions found in the formulation. This could provide tighter convex regions for bilinear terms depending on the value of the parameter α.

(b) Optimization solver

The Branch and Reduce Optimization Navigator (BARON) was the chosen optimization in this work to yield global optimal solutions for the presented case studies. As discussed in Section 2.2.5 of Chapter 2, BARON uses a LP-based branch and bound based algorithm which annexes duality techniques to reduce the size of the model during the solution process. Its robustness lies in its ability to solve a wide range of optimization problems and handle various nonlinear functions. Its solution algorithm can often guarantee global solutions of nonconvex problems and does not require initialization of variables (Sahinidis, 2014). However, the major challenge encountered with BARON 14.0.3 was the use large number of nodes between two optimal points during its search for the global optimal value. Hence, the solution procedure was terminated by limiting the computational time to a certain extent at the expense of stopping at a local optimal point.

During online process optimization, i.e. optimization performed during plant operation, the main goal is to determine key variables which have a major effect on the objective function and providing improved plant performance in minimum CPU time. Global optimality becomes of greater essence when plant design is still being undertaken. Marginal values in mathematical programming tell the modeller the extent to which all variables affect the objective function. This further allows the determination of critical variables, i.e. variables which should be manipulated by the process engineer to get greater saving in water for instance or greater improvement in plant profit. However, BARON 14.0.3 did not provide marginal values for the models solved in this work. Hence such information could not be provided which forms another limitation of this work.

The performance of BARON 14.0.3 could be improved by revisiting of the proposed formulation, tightening or adding bounds on certain variables and exploring possible ways of further reduction in model size. This entails removing redundant constraints if existent or reducing the number of both continuous and binary variables by reformulating some constraints in the model. Scaling of variables could also be useful to reduce the CPU time by ensuring that the magnitudes of variables are within the same order (GAMS Development Corp., 2014). It is worth pointing out that the features of BARON solver have been enhanced in its latest version, i.e. BARON 17.4.1. For instance, BARON 17.4.1 allows its MIP subsolver to use multiple cores simultaneously to decrease the CPU time since most of the solution time is spent on solving MIP relaxations. The use of multiple cores is translated into the simultaneous use of multiple processors amenable to parallel computing (Sahinidis, 2017). Furthermore, some other MINLP solvers discussed in Chapter 2 should be tested on the presented formulation to assess their efficacy compared to BARON. DICOPT, for instance, allows the user to choose MIP and NLP solvers that will give the best computational performance for a given model. NLP solvers used in DICOPT often requires the initialization of variables involved in nonlinear terms which, if

adequately chosen, can drastically reduce CPU time for large scale problems (GAMS Development Corp., 2014).

(c) Pre-processing techniques

Pre-processing techniques are usually built-in functions in many MINLP solvers. They aim to improve a given formulation by analysing each constraint, identify any infeasibility or redundancy and improve bounds to reduce the optimization search space (Savelsbergh, 1994). Additional pre-processing can also be applied to the model prior to attempting to solve it in order to reduce the computational time. For instance, a graphical targeting technique could be used as a pre-processing step for the proposed formulation to determine the optimum value of some variables such as the removal ratio of the ED process without increasing the computational burden. The resultant water network from graphical targeting can also be used as a starting point for mathematical optimization to reduce the CPU time.

(d) Design model of the electrodialysis process

The complexity of the electrodialysis design sub-model is a major contributor the high CPU time of the proposed formulation. In published literature, researchers have opted for black-box approaches to model regeneration units due to their simplicity. Blackbox models are usually made of linear equations, hence they can greatly contribute to the reduction of the CPU time. However, the CPU time is usually reduced at the expense of losing accuracy on the costing of the water network. It is worth reiterating that the merit of the proposed formulation resides in its ability to provide the modeller with the optimum sizes of the regenerator while enabling the minimization of its energy consumption. Blackbox approaches, on the other hand, focus on optimizing the cost of regeneration by manipulation performance indices such as feed flowrate and removal ratio. This usually results in an underestimated overall cost of the regeneration process. It is therefore recommended to find a middle way between black-box and detailed modelling approaches as a strategy for CPU

time improvement. In other words, the development of a simplified ED can design model which has the ability to capture the merits of both modelling strategies should be the subject of future research studies.

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7

CONCLUDING REMARKS

The work presented in this dissertation focused on developing a mathematical formulation for the minimization of freshwater use in batch water networks with a single key contaminant. The water network comprised washing operations, a buffer system with two storage tanks and an embedded regeneration system. The technique considered short-term scheduling of batch plants which forms the platform for the synthesis of the water network. The simultaneous optimization of scheduling and water use yielded the optimum schedule that is concomitant with the minimum freshwater usage. The regenerator system was designed with sufficient details to enable the determination of its size and quantification of its energy consumption, allowing an accurate costing of the water network.

The formulation was validated using two illustrative examples and an industrial process. In all cases, the formulation yielded large-scale MINLP models. A reduction in freshwater intake of 37 % and 41 % were respectively achieved in both industrial examples while maintaining a maximum production. The schedule of each plant was generated and details on the batch size and the optimum sequences of tasks were given for each processing unit. The design specifications of the ED treatment units and their optimum consumption of energy were also obtained. The industrial case study aimed to test the practicality of the developed formulation by exploring reuse

opportunities in the RMRD section of Amul, a dairy based in India. The freshwater usage was reduced by 37 % and a modified plant schedule was suggested. An economic analysis was performed on the optimized plant and a reduction in operating cost of 20 % was observed.

The presented technique is limited to single contaminant cases which are very seldom in the process industry and the regeneration system only allows the removal of ionic contaminants through electrodialysis. Furthermore, optimum solutions are generated in a considerably high CPU time. It is therefore recommended that future work focuses on extending this formulation to account for multiple contaminants and medium to long-term scheduling which involves cyclic production. An enhancement of regeneration system is also required to include a network of distinct wastewater treatment technologies and facilitate the removal of various contaminants. Although the current work focusses on the usage of water as a mass separating agent (MSA), it can be readily adjusted to cater for both mass transfer and non-mass transfer-based operations. A substantial effort should be directed towards reducing the computational time of optimization solvers by adopting pre-processing and relaxation techniques that alleviate the complexity of the proposed formulation. Nonetheless, this work provides a solid basis for future research to develop improved wastewater minimization techniques for multipurpose batch plants.

Appendices

Appendix A: Scheduling formulation of Seid and Majozi (2012)

The scheduling model of Seid and Majozi (2012) is based on the SSN representation of Majozi and Zhu (2001). It was developed for multipurpose batch plants aiming at maximizing the profit of the plant or minimizing the makespan and obtain a plant schedule with an optimized utilization of resources. The following data need to be known prior to optimization.

(i) The production recipe which indicate the sequence of tasks for the conversion of raw materials into products
(ii) The capacity of each unit, the type and number of task each unit can process.
(iii) The maximum storage capacity of all materials
(iv) The time horizon of interest

The mathematical formulation includes the following constraints.

A.1 Allocation constraint

Constraint (A.1) states that only one task can be active in a unit at any given time slot *p*.

$$\sum_{s_j^{in} \in S_{in,j}^*} y\left(s_j^{in}, p\right) \leq 1 \qquad \forall\ j \in J,\ p \in P \qquad \text{(A.1)}$$

A.2 Capacity constraint

Constraint (A.2) ensures that the amount of batch processed in a unit at any given slot *p* does not exceed the capacity of the unit. $V^{L}_{s^{in}_{j}}$ and $V^{U}_{s^{in}_{j}}$ represents the lower and upper capacity limits for the batch size of a given material state s^{in}_{j}.

$$V^{L}_{s^{in}_{j}} y\left(s^{in}_{j}, p\right) \le m_u\left(s^{in}_{j}, p\right) \le V^{U}_{s^{in}_{j}} y\left(s^{in}_{j}, p\right) \qquad \forall\ j \in J,\ p \in P,\ s^{in}_{j} \in S^{in}_{j} \tag{A.2}$$

A.3 Material balance for storage

Constraint (A.3) states that the amount of material *s* stored at any slot *p* is as the amount that was previously stored at slot *p-1* adjusted to an amount resulting from the difference between the portion of state *s* produced at slot *p-1* and the portion used at the current slot *p*. Constraint (A.4) represents the storage balance for product s^p. It ensures that, at any given slot *p*, the amount of product produced adds up to the amount that was present in storage at slot *p-1* to give the total amount of product stored at time slot *p*.

$$q_s(s, p) = q_s(s, p-1) - \sum_{s^{in}_{j} \in S^{sc}_{in,j}} \rho^{sc}_{s^{in}_{j}} m_u\left(s^{in}_{j}, p\right) + \sum_{s^{in}_{j} \in S^{sp}_{in,j}} \rho^{sp}_{s^{in}_{j}} m_u\left(s^{in}_{j}, p-1\right) \qquad \forall\ s \in S,\ p \in P \tag{A.3}$$

$$q_s\left(s^p, p\right) = q_s\left(s^p, p-1\right) + \sum_{s^{in}_{j} \in S^{s^p}_{in,j}} \rho^{sp}_{s^{in}_{j}} m_u\left(s^{in}_{j}, p\right) \qquad \forall\ p \in P,\ s^p \in S^p \tag{A.4}$$

A.4 Duration constraint: Duration as a function of batch size

The duration of a task in a particular processing unit is given by Constraint (A.5). It is defined as the time difference between its starting and finishing time and is dependent on the batch size.

$$t_p\left(s_j^{in}, p\right) \geq t_u\left(s_j^{in}, p\right) + \alpha\left(s_j^{in}\right) y\left(s_j^{in}, p\right) + \beta\left(s_j^{in}\right) m_u\left(s_j^{in}, p\right)$$
$$\forall \;\; j \in J,\; p \in P,\; s_j^{in} \in S_j^{in} \qquad \text{(A.5)}$$

A.5 Sequence constraints

A.5.1 Same task in the same unit

Constraint (A.6) ensures that a batch starts being processed in a unit at slot *p* after the completion of the previous batch in the same unit at the previous time slot *p-1*. In this case, both batches are of the same nature, i.e. they are made of the same material state.

$$t_u\left(s_j^{in}, p\right) \geq t_p\left(s_j^{in}, p-1\right) \qquad \forall\; j \in J,\, p \in P, s_j^{in} \in S_{in,j}^{*} \qquad \text{(A.6)}$$

A.5.2 Different tasks in the same unit

Similar to Constraint (A.6), Constraint (A.7) ensures that a task start being processed in a unit after all the previous tasks are completed. This constraint looks at a case were different tasks can occur in the same unit.

$$t_u\left(s_j^{in}, p\right) \geq t_p\left(s_j^{in'}, p-1\right) \qquad \forall\; j \in J,\; p \in P, s_j^{in} \neq s_j^{in'}, s_j^{in}, s_j^{in'} \in S_{in,\,j}^{*} \qquad \text{(A.7)}$$

A.5.3 Different tasks in different units

(a) If an intermediate state is produced from one unit

Constraint (A.8) ensures that an intermediate state produced in a unit does not exceed its storage capacity if it is produced at time slot *p-1* but not consumed in another unit at time slot *p*, i.e. *t(j,p)=0*. If both the producing and consuming task are active at consecutive time slots, then the amount of intermediate state stored will be less than

the amount produced. The binary variable *t(j,p)* will then takes a value of 1 and Constraint (A.9) will hold. Constraint (A.9) ensures that the consuming task of an intermediate state start after the completion of its producing task.

$$\rho^{sp}_{s^{in}_j} m_u\left(s^{in}_j, p-1\right) \le q_s(s,p) + V^U_j t(j,p)$$
$$\forall\ j \in J,\ p \in P, s^{in}_j \in S^{sp}_{in,j} \tag{A.8}$$

$$t_u\left(s^{in}_{j'}, p\right) \ge t_p\left(s^{in}_j, p-1\right) - H\left(2 - y\left(s^{in}_j, p-1\right) - t(j,p)\right)$$
$$\forall\ j \in J,\ p \in P, s^{in}_j \in S^{sp}_{in,j}, s^{in}_{j'} \in S^{sc}_{in,j'} \tag{A.9}$$

(b) If an intermediate state is produced from more than one unit

Constraint (A.10) states that the amount of state consumed by a task can either come from storage or directly from its producing units. Depending whether *t(j,p)*=0 or *t(j,p)*=1 as explained earlier, Constraint (A.9) will also be used for sequencing in this category. Constraint (A.11) ensures that the starting time of a task consuming an intermediate state occurs after the completion of all the producing tasks which occurred at pervious time slots. This constraint ensures adequate sequencing between non-consecutive tasks consuming and producing an intermediate material. In this case, the producing task occurred at slot *p-2* and the consuming task is occurring at the current slot *p*.

$$\sum_{s^{in}_j \in S^{sc}_{in,j}} \rho^{sc}_{s^{in}_j} m_u\left(s^{in}_j, p\right) \le q_s(s, p-1) + \sum_{s^{in}_j \in S^{sp}_{in,j}} \rho^{sp}_{s^{in}_j} m_u\left(s^{in}_j, p-1\right) t(j,p)$$
$$\forall\ \boldsymbol{j \in J,\ p \in P} \tag{A.10}$$

$$t_u\left(s^{in}_{j'}, p\right) \ge t_p\left(s^{in}_j, p-2\right) - H\left(1 - y\left(s^{in}_j, p-2\right)\right)$$
$$\forall\ j \in J,\ p \in P, s^{in}_j \in S^{sp}_{in,j}, s^{in}_{j'} \in S^{sc}_{in,j'} \tag{A.11}$$

A.6 Sequence constraints for FIS policy

Constraint (A.12) ensures that the amount of intermediate state stored at any point in time does not exceed the available storage capacity. The binary variable *x(s,p)* indicates the availability (*x(s,p)*=1) or absence of storage (*x(s,p)*=0) for intermediate sate s at time slot *p*. Constraint (A.13) states that the finishing time of the producing task should coincide with the starting time of the consuming task of state *s* provided that no storage is available for this state, i.e. *x(s,p)*=0. This constraint is relaxed if there is an available storage for intermediate state *s*, i.e. *x(s,p)*=1.

$$\sum_{s_j^{in} \in S_{in,j}^{sp}} \rho_{s_j^{in}}^{sp} m_u\left(s_j^{in}, p-1\right) + q_s(s, p-1) \le QS^U + \sum_{j \in J_s} V_j^U (1 - x(s, p))$$
$$\forall\ j \in J,\ p \in P, s \in S \qquad \text{(A.12)}$$

$$t_u\left(s_{j'}^{in}, p\right) \le t_p\left(s_j^{in}, p-1\right) + H\left(2 - y\left(s_{j'}^{in}, p\right) - y\left(s_j^{in}, p-1\right)\right) + H\left(x(s, p)\right)$$
$$\forall\ j \in J,\ p \in P, s_j^{in} \in S_{in,j}^{sp}, s_{j'}^{in} \in S_{in,j}^{sc}, s \in S \qquad \text{(A.13)}$$

A.7 Storage constraints

Constraint ((A.14) indicates that the amount of state s stored should not exceed the maximum capacity of the available storage. The storage capacity for state *s* in this case includes the capacity of both its dedicated storage tank and its producing units. Constraint ((A.15) ensures that intermediate materials are stored in their producing units at consecutive time slots. Constraint ((A.16) ensures that a unit being utilized for a temporary storage of an intermediate material at time slot *p* is not assigned to process any task at that time slot.

$$q_s(s, p) \le QS^U + \sum_{s_j^{in} \in S_{in,j}^{sp}} u\left(s_j^{in}, p\right) \qquad \forall\ j \in J,\ p \in P, s \in S \qquad \text{(A.14)}$$

$$u\left(s_j^{in}, p\right) \le \rho_{s_j^{in}}^{sp} m_u\left(s_j^{in}, p-1\right) + u\left(s_j^{in}, p-1\right) \quad \forall\ j \in J,\ p \in P, s_j^{in} \in S_{in,j}^{sp} \qquad \text{(A.15)}$$

$$u\left(s_j^{in}, p\right) \le V_j^U - \left(1 - \sum_{s_j^{in} \in S_{in,j}^*} y\left(s_j^{in}, p\right)\right) \qquad \forall\ j \in J,\ p \in P,\ s_j^{in} \in S_{in,j}^{sp} \tag{A.16}$$

A.8 Tightening constraints

Constraint (A.17) is used to ensure that all tasks processed by a given unit occur within the time horizon. It states that the sum of the duration of all tasks processed in a unit should not exceed the length of the time horizon. For the purpose of this work, Constraint (A.17) was modified into Constraint (A.18) to also cater for the duration of washing operations in the tightening constraints. This is due to the fact that a washing operation is scheduled to occur after a batch task has been completed.

$$\sum_{s_j^{in} \in S_{in,j}^*} \sum_{p} \tau\left(s_j^{in}, p\right) y\left(s_j^{in}, p\right) + \beta\left(s_j^{in}, p\right) m_u\left(s_j^{in}, p\right) \le H \tag{A.17}$$

$$\forall\ j \in J$$

$$\sum_{s_j^{in} \in S_{in,j}^*} \sum_{p} \begin{matrix} \tau\left(s_j^{in}, p\right) y\left(s_j^{in}, p\right) + \tau^w\left(s_j^{in}, p\right) y\left(s_j^{in}, p\right) \\ + \beta\left(s_j^{in}, p\right) m_u\left(s_j^{in}, p\right) \end{matrix} \le H \tag{A.18}$$

$$\forall\ j \in J$$

A.9 Time horizon constraints

Constraint ((A.19) and ((A.20) ensures that the starting and finishing time of all the tasks occur within the time horizon of interest

$$t_u\left(s_j^{in}, p\right) \le H \qquad \forall\ j \in J, p \in P, s_j^{in} \in S_j^{in} \tag{A.19}$$

$$t_p\left(s_j^{in}, p\right) \le H \qquad \forall\ j \in J,\ p \in P, s_j^{in} \in S_j^{in} \tag{A.20}$$

A.10 Nomenclature

The following sets, parameters and variables are used in the scheduling formulation of Seid and Majozi (2012).

Sets

P	$\{ p \mid p$ represents a time point$\}$
J	$\{ j \mid j$ denotes a unit$\}$
S	$\{ s \mid s$ represent any state other than a product$\}$
S^P	$\{ s^P \mid s^P$ represent any state other than a product$\}$
S_j^{in}	$\{ s_j^{in} \mid s_j^{in}$ is an effective state representing a task performed in unit $j\}$
$S_{in,j}^{sc}$	$\{ s_{in,j}^{sc} \mid s_{in,j}^{sc}$ task which consumes state $s\}$
$S_{in,j}^{*}$	$\{ s_{in,j}^{*} \mid s_{in,j}^{*}$ task performed in unit $j\}$
$S_{in,j}^{sp}$	$\{ s_{in,j}^{sp} \mid s_{in,j}^{sp}$ task which produce a state s other than a product$\}$
$S_{in,j}^{S^P}$	$\{ s_{in,j}^{S^P} \mid s_{in,j}^{S^P}$ task producing a state which is a product$\}$

Parameters

V_j^U	capacity of unit j
$V_{s_j^{in}}^U$	maximum capacity of unit j to process a task
$V_{s_j^{in}}^L$	minimum capacity of unit j to process a task
H	time horizon of interest
QS^o	initial amount of state s found in storage

QS^U	maximum storage capacity for state *s*
$\tau\left(s_j^{in}\right)$	duration of a processing task in unit *j*
$\beta\left(s_j^{in}\right)$	duration of a processing task in unit *j*
$\tau^w\left(s_j^{in}\right)$	duration of washing in unit *j*
$\rho\left(s_{in,j}^{sp}\right)$	portion of state *s* produced by a task
$\rho\left(s_{in,j}^{sc}\right)$	portion of state *s* consumed by a task

Variables

$mu\left(s_j^{in}, p\right)$	amount of material processed by a task at time slot *p*
$u\left(s_j^{in}, p\right)$	amount of material stored in unit *j* at time slot *p*
$t^u\left(s_j^{in}, p\right)$	starting time of a task at time slot *p*
$t^p\left(s_j^{in}, p\right)$	finishing time of a task at time slot *p*
$y\left(s_j^{in}, p\right)$	binary variable associated with the assignment of a task at time slot *p*
$x(s, p)$	binary variable associated with the availability of storage assignment of a task at time slot *p*
$q_S(s, p)$	amount of state *s* stored at time slot *p* binary variable associated with the assignment of a task at time slot *p*
$t(j, p)$	binary variable associated with the usage of a state produced by unit *j* at time slot *p*

References

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