

**WASTEWATER MINIMIZATION IN MULTIPURPOSE
BATCH PLANTS WITH A REGENERATION UNIT:
MULTIPLE CONTAMINANTS**



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WASTEWATER MINIMIZATION IN MULTIPURPOSE BATCH PLANTS WITH A REGENERATION UNIT: MULTIPLE CONTAMINANTS

by

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SYNOPSIS

The generation of wastewater in processing industries is an inevitable activity since almost all operations require water at some point. Process equipment cleaning is a universal wastewater generating operation as it is practiced in all segments of manufacturing industries. This is especially important in batch plants due to inherent sharing of equipment by different tasks. Wastewater minimization can be achieved by employing water reuse opportunities. In the past, an optimal batch schedule was assumed before the minimization of wastewater, which was an oversimplification of the problem. This is because the batch schedule impacts on the starting and finishing times of water-using operations, hence any wastewater target obtained is specific to the schedule given. This dissertation presents a methodology to address the problem of wastewater minimization by extending the concept of water reuse to include a wastewater regenerator. The regenerator purifies wastewater to such a quality that it can be reused in other operations. This further increases water reuse opportunities in the plant, thereby significantly reducing freshwater demand and effluent generation. The mathematical model presented determines the optimum batch production schedule that achieves the minimum wastewater generation within the same framework. The effectiveness of the method was demonstrated in its application to two case studies involving multiple contaminants and wastewater reductions of 19.2% and 26% were achieved.

Keywords: wastewater minimization, regeneration, multiple contaminants

DECLARATION

I, Omobolanle Adekola, student number 24241688, declare that:

1. I understand what plagiarism is and am aware of the University's policy in this regard.
2. I declare that this dissertation is my own original work. Where other people's work has been used (either from a printed source, internet or any other source), this has been properly acknowledged and referenced in accordance with departmental requirements.
3. I have not used work previously produced by another student or any other person to hand in as my own.
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5. The work presented in this dissertation has not been submitted anywhere else in partial or full fulfillment of another degree.

Student_____

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NOMENCLATURE LIST

Sets

P	$\{ p \mid p = \text{time point} \}$
J	$\{ j \mid j = \text{unit} \}$
C	$\{ c \mid c = \text{contaminant} \}$
S_{in}	$\{ s_{in} \mid s_{in} = \text{input state into any unit} \}$
S_{out}	$\{ s_{out} \mid s_{out} = \text{output state from any unit} \}$
S	$\{ s \mid s = \text{any state} \} = S_{in} \cup S_{out}$
$S_{in,j}$	$\{ s_{in,j} \mid s_{in,j} = \text{input state into unit } j \} \subseteq S_{in}$
$S_{in,j}^*$	$\{ s_{in,j}^* \mid s_{in,j}^* = \text{input state into unit } j \} \subseteq S_{in}$
$S_{out,j}$	$\{ s_{out,j} \mid s_{out,j} = \text{output state from unit } j \} \subseteq S_{out}$

Variables associated with wastewater minimization

$mw_{in}(s_{out,j}, p)$	mass of water into unit j for cleaning state s_{out} at time point p
$mw_{out}(s_{out,j}, p)$	mass of water produced at time point p from unit j
$mw_f(s_{out,j}, p)$	mass of freshwater into unit j at time point p
$mw_e(s_{out,j}, p)$	mass of effluent water from unit j at time point p
$mw_r(s_{out,j}, s_{out,j'}, p)$	mass of water recycled to unit j' from j at time point p
$ms_{in}(s_{out,j}, p)$	mass of water transferred from unit j to storage at time point p
$ms_{out}(s_{out,j}, p)$	mass of water transferred from storage to unit j at time point p
$mreg_{in}(s_{out,j}, p)$	mass of water transferred from storage to regenerator at time point p
$mreg_{out}(s_{out,j}, p)$	mass of water transferred from regenerator to unit j at time point p
$m_{dirt}(c, p)$	mass of contaminant c removed from water by regenerator

	at time point p
$c_{in}(s_{out,j}, c, p)$	inlet concentration of contaminant c , to unit j at time point p
$c_{out}(s_{out,j}, c, p)$	outlet concentration of contaminant c , from unit j at time point p
$cs_{in}(c, p)$	inlet concentration of contaminant c , to storage at time point p
$cs_{out}(c, p)$	outlet concentration of contaminant c , from storage at time point p
$cr_{out}(c, p)$	outlet concentration of contaminant c , from regenerator at time point p
$qw_s(p)$	amount of water stored in storage at time point p
$t_{out}(s_{out,j}, p)$	time at which a state is produced from unit j at time point p
$tw_{in}(s_{out,j}, p)$	time at which water is used at time point p in unit j
$tw_{out}(s_{out,j}, p)$	time at which water is produced at time point p from unit j
$tw_r(s_{out,j}, s_{out,j'}, p)$	time at which water is recycled from unit j to unit j' at time point p
$ts_{in}(s_{out,j}, p)$	time at which water is transferred from unit j to storage at time point p
$ts_{out}(s_{out,j}, p)$	time at which water is transferred from storage to unit j at time point p
$treg_{in}(s_{out,j}, p)$	time at which water is transferred from storage to regenerator at time point p
$treg_{out}(s_{out,j}, p)$	time at which water is transferred from regenerator to unit j at time point p
$yw_r(s_{out,j}, s_{out,j'}, p)$	binary variable showing transfer of water from unit j to unit j' at time point p
$yw(s_{out,j}, p)$	binary variable showing usage of water in unit j at time point p
$ys_{in}(s_{out,j}, p)$	binary variable showing transfer of water from unit j to storage at time point p
$ys_{out}(s_{out,j}, p)$	binary variable showing transfer of water from storage to unit j at time point p

$yreg_{in}(s_{out,j}, p)$	binary variable showing transfer of water from storage to regenerator at time point p
$yreg_{out}(s_{out,j}, p)$	binary variable showing transfer of water from regenerator to unit j at time point p

Variables associated with production scheduling

$t_{out}(s_{out,j}, p)$	time at which a state is produced from unit j at time point p
$t_{in}(s_{in,j}, p)$	time at which a state is used in or enters unit j at time point p
$q_s(s, p)$	amount of state s stored at time point p
$m_{out}(s_{out,j}, p)$	amount of state produced from unit j at time point p
$m_{in}(s_{in,j}, p)$	amount of state used in or enters unit j at time point p
$y(s_{in,j}^*, p)$	binary variable associated with usage of state s at time point p
$d(s, p)$	amount of state delivered to customers at time point p

Parameters associated with wastewater minimization

CE	cost of effluent water treatment (c.u./kg water)
CF	cost of freshwater (c.u./kg water)
$M(s_{out,j}, c)$	mass load of contaminant c added from unit j to the water stream
$Mw^U(s_{out,j})$	maximum inlet water mass of unit j
$C_{in}^U(s_{out,j}, c)$	maximum inlet concentration of contaminant c in unit j
$C_{out}^U(s_{out,j}, c)$	maximum outlet concentration of contaminant c from unit j
$CS_{out}^o(c)$	initial concentration of contaminant in storage
$CS_{out}^U(c)$	maximum outlet concentration of contaminant c from storage
$CR_{out}^U(c)$	maximum outlet concentration of contaminant c from regenerator
$RR(c)$	removal ratio of contaminant c from regenerator
Qw_s^o	initial amount of water in storage



Qw_s^U	maximum capacity of storage
$\tau w(s_{out,j})$	mean processing time of unit j
f_{reg}	regenerator flowrate

Parameters associated with production scheduling

V_j^U	maximum design capacity of a particular unit j
V_j^L	minimum design capacity of a particular unit j
$\tau(s_{in,j}^*)$	mean processing time for a state
$Q_s^0(s)$	initial amount of state s stored
$Q_s^U(s)$	maximum amount of state s stored within the time horizon of interest
$CP(s)$	selling price of product s , s = product
H	time horizon of interest

CHAPTER 1

INTRODUCTION

1.1 Background

Wastewater minimization has become an important topic of research, driven by the rising costs of freshwater and effluent treatment, more stringent environmental legislation, increased environmental awareness and the drive for more sustainable practices. Many published works have been dedicated to investigating techniques for wastewater minimization in continuous processes due to their occurrence in chemical and petrochemical industries and their association with large quantities of water. Usually in literature, the first step in accomplishing wastewater minimization is through water targeting. Targeting determines the minimum freshwater and wastewater flowrates that can be achieved after water reuse/recycle opportunities within a process plant have been employed. This is followed by the synthesis of the network corresponding to the established targets.

Wastewater regeneration has been widely accepted as an effective means to reduce wastewater generation further and is usually employed after the opportunities for reuse/recycle have been exhausted. Here, water reuse refers to the use of an outlet wastewater stream from a processing unit in another processing unit while recycle refers to the reuse of an outlet wastewater stream from a processing unit in the same unit. Wastewater regeneration refers to the purification of water to such an extent that it can be reused by water-using operations, thus reducing the requirement for freshwater.

Batch processes are now commonly used for the manufacture of specialty chemicals, due to their flexibility such that the configuration of a batch plant can be easily modified to meet product demand. These processes are found in pharmaceutical, agrochemical and food industries. The nature of a batch process is such that tasks have distinct starting and finishing times with a finite duration. Consequently, material flows are time dependent and direct application of wastewater minimization methods for continuous processes to batch processes is not readily appropriate. Literature on wastewater minimization in batch processes, though limited in comparison to their continuous counterparts, has addressed topics like direct

reuse/recycle, indirect reuse in the form of wastewater storage and regeneration for wastewater minimization. The majority of these works have utilized mathematical optimization techniques as opposed to graphical/numerical techniques to solve the problem in batch processes, due to the added complexity associated with time and multiple contaminants.

1.2 Motivation

In the past, an optimal batch schedule was assumed before the minimization of wastewater, which was an oversimplification of the problem. This is because the batch schedule impacts on the starting and finishing times of water-using operations, hence any wastewater target obtained was specific to the schedule given. Another approach that has been utilized in literature is the sequential approach whereby the results obtained from optimization of the batch schedule were used for the optimization of the water network equivalent to minimum wastewater production. The best model is one that simultaneously determines a cost optimal schedule that fulfils the batch production requirement as well as the minimum wastewater production. Majozi and Gouws (2009) presented a mathematical optimization methodology that optimized the batch production schedule and minimized wastewater production simultaneously. In this situation, the starting and finishing times of the batch processes were optimization variables. This work, however, did not consider regeneration to reduce the overall wastewater target further.

1.3 Aim

The above discussion highlights the need for a wastewater minimization methodology that incorporates wastewater regeneration in batch plants. Moreover, the batch production schedule and water network that correspond to minimum water requirement ought to be determined simultaneously within the same optimization framework. This dissertation is aimed at addressing this particular problem. The work by Majozi and Gouws (2009) is extended to include regeneration.

1.4 Problem statement

The problem addressed can be stated as follows:

Given:

- (i) the production recipe for each product, including mean processing times in each unit operation,
- (ii) the available units and their capacities,
- (iii) the necessary costs and stoichiometric data,
- (iv) the contaminant mass load of each contaminant,
- (v) the water requirement and cleaning duration for each unit to achieve the required cleanliness,
- (vi) maximum inlet and outlet concentrations of each contaminant,
- (vii) the maximum storage available for water reuse,
- (viii) the performance of the regenerator and
- (ix) the time horizon of interest,

Determine:

the production schedule that achieves the minimum amount of wastewater generated by exploring recycle and reuse opportunities in the presence of a central storage vessel and a wastewater regenerator.

1.5 Structure

This dissertation is divided as follows: Chapter 2 discusses literature relevant to wastewater minimization with a focus on regeneration. Chapter 3 presents the proposed wastewater minimization methodology. In Chapter 4, the applicability of the methodology to two case studies is demonstrated. Finally, in Chapter 5 the conclusions drawn from the application of the methodology are discussed. A recommendation is also presented in this chapter.



Reference

Majozi, T., & Gouws, J.F. (2009). A mathematical optimisation approach for wastewater minimisation in multipurpose batch plants: Multiple contaminants. *Comput. Chem. Eng.*, 33, 1826-1840

CHAPTER 2

LITERATURE REVIEW

Introduction

This chapter presents a review of literature pertaining to wastewater minimization in batch processes. Wastewater minimization methodologies for continuous processes have been well documented in literature. Furthermore, these methodologies have provided many useful insights in addressing the same problem in batch processes. A good starting point in this chapter therefore, is a brief discussion of methodologies for continuous processes. Some important issues that will be extracted are:

- the nature of the problem addressed, i.e. fixed load/fixed flowrate problems
- applicability of the method to single or multiple contaminant problems
- whether or not a treatment or regeneration unit is considered

These issues are discussed forthwith to facilitate understanding. In fixed load problems, the water-using operations are modeled as mass-transfer based operations, i.e., water is used as a mass separating agent. The contaminant concentration of the water changes due to the mass load of contaminant picked up. The maximum allowable inlet and outlet concentrations of the operations are specified. Examples are washing and extraction operations. In fixed flowrate problems, the concern is not about the mass transfer of contaminants but the flowrate of water. The inlet and outlet flowrates of the operations, which may not be equal, are specified. These operations may be modeled with outlet streams leaving at a specified concentration, while the inlet streams have a maximum allowable concentration. Cooling towers, boilers and reactors can be modeled this way.

Single contaminant streams have been assumed in problems for simplicity, though multiple contaminant systems are more readily encountered in industry. However, there are certain practical situations where the assumption of a single contaminant is applicable, e.g. the pulp and paper industry where suspended solids are modeled as a single contaminant (Bagajewicz

and Savelski, 2001). Also found in literature is the grouping of contaminants with similar properties together as a single pseudo-contaminant, to distinguish them from species with different properties. Other pollutants can be ignored if their concentrations are too low (Bagajewicz, 2000).

Wastewater treatment differs from wastewater regeneration with regard to the final destination of treated water. Wastewater treatment refers to the purification of water to a concentration level acceptable by legislation, for discharge to the environment. Regeneration refers to the purification of water to such an extent that it can be reused by water-using operations, thus reducing the requirement for freshwater.

The second section of this chapter is dedicated to wastewater minimization methodologies for batch processes. An important issue that goes hand in hand with this topic is batch process scheduling. A brief discussion on the concepts of scheduling techniques and their impact on wastewater minimization methodologies in batch processes will be presented in this section.

Existing methodologies for wastewater minimization in both continuous and batch processes can be broadly divided into two groups, namely, graphical/numerical techniques based on pinch analysis and mathematical optimization techniques. The main advantage of graphical pinch analysis techniques is that, the various water network targets such as freshwater and wastewater flowrates and the pinch location can be identified beforehand. These are used as guidelines during network synthesis. A drawback however, is that these techniques are often limited to problems with a single contaminant. Mathematical optimization techniques on the other hand can handle multiple contaminant problems, are flexible in the definition of the objective function, but do not provide the same insights as the graphical techniques. Also, when the resulting mathematical formulation is in the form of a nonconvex, nonlinear program, NLP or a nonconvex, mixed integer nonlinear program, MINLP, finding the global solution may be a challenge.

2.1 Graphical techniques for wastewater minimization in continuous processes

Wang and Smith (1994) pioneered research in wastewater minimization using graphical pinch analysis, whereby the minimum wastewater target of a system of water-using operations, which exploited recycle and reuse, could be obtained. The method, applicable to fixed load problems, was a special case of the concept of mass exchange between rich streams and lean streams, developed by El-Halwagi and Manousiouthakis (1989). On a plot of concentration against mass load, a limiting composite curve was constructed. Against this curve, a water supply line was matched and the inverse of the slope of this line gave the freshwater and wastewater target. The freshwater and wastewater targets were equal because there was no loss or gain of water. An illustration is provided in Figure 2.1. In the figure, freshwater was used, hence the water supply line went through the coordinate (0, 0). The water pinch was located on the plot as the point that limited the slope of the water supply line.

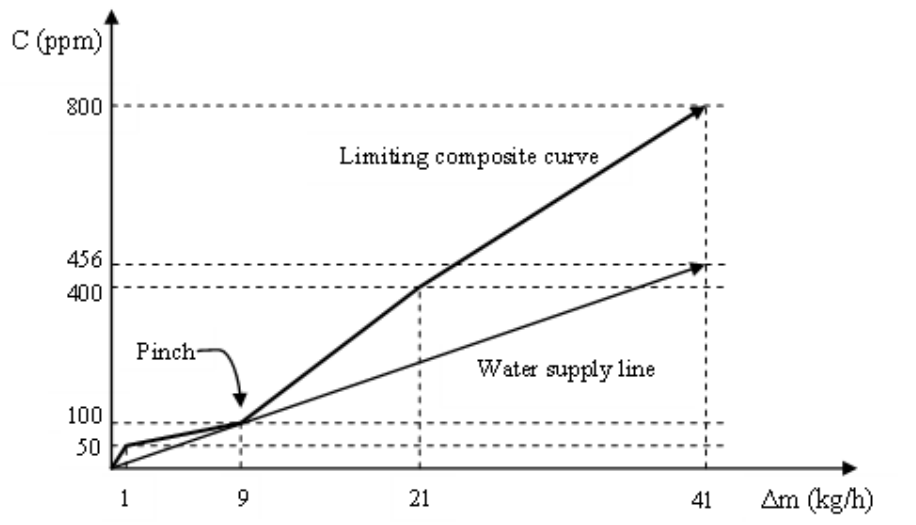


Figure 2.1: Limiting composite curve

Next, the water network corresponding to the determined target was synthesized using a method analogous to the heat exchanger network design by Linnhoff and Hindmarsh (1983). The advantage of the method by Wang and Smith (1994) was that the minimum wastewater (or freshwater) target was obtained before network synthesis. Drawbacks of this method were

that more complex constructions of limiting composite curves were required to address multiple contaminants. Secondly, the method was only applicable to fixed load problems. Thirdly, as pointed out by Ulson de Souza *et al.* (2009), in some scenarios during network synthesis, operations had to be divided in order to achieve the established targets. In reality, operation divisions are impossible. These drawbacks gave rise to several modifications and advancements to the work of Wang and Smith (1994).

Dhole *et al.* (1996) proposed a method suitable for fixed flowrate problems. In this method, all inlet streams were defined as demands and all outlet and freshwater streams were defined as sources. This allowed units with multiple inlet or outlet streams to be modeled effectively. In this technique, two separate curves representing the source and demand composites were plotted on a contaminant concentration vs. flowrate graph. The water pinch was the point where the two composite curves touched. This pinch point however could be adjusted by mixing different source streams together. This meant that many local flowrate targets could be identified. Unless the correct mixing was identified, there was no guarantee that the targets obtained were minima. To obtain the minimum flowrate targets, numerous trial and error exercises were performed. As pointed out by Hallale (2002), this mixing should ideally be performed in the network synthesis stage. To address the limitations of the method, Hallale (2002) developed the water surplus diagram as a new targeting approach also applicable to fixed flowrate problems.

In the method by Hallale (2002), a plot similar to that by Dhole *et al.* (1996) was utilized. In the plot, regions where the source composite curve was above the demand composite curve (water surplus regions) and vice versa (water deficit regions) were identified. The amount of water surplus or deficit in each region could be determined by calculating the area enclosed by each rectangle representing the region. Next, cumulative values of the water surplus and water deficit were plotted on a water purity vs. flowrate graph such that the water surplus values were positive and the water deficit values were negative. This new plot was the water surplus diagram. An example is provided in Figure 2.2.

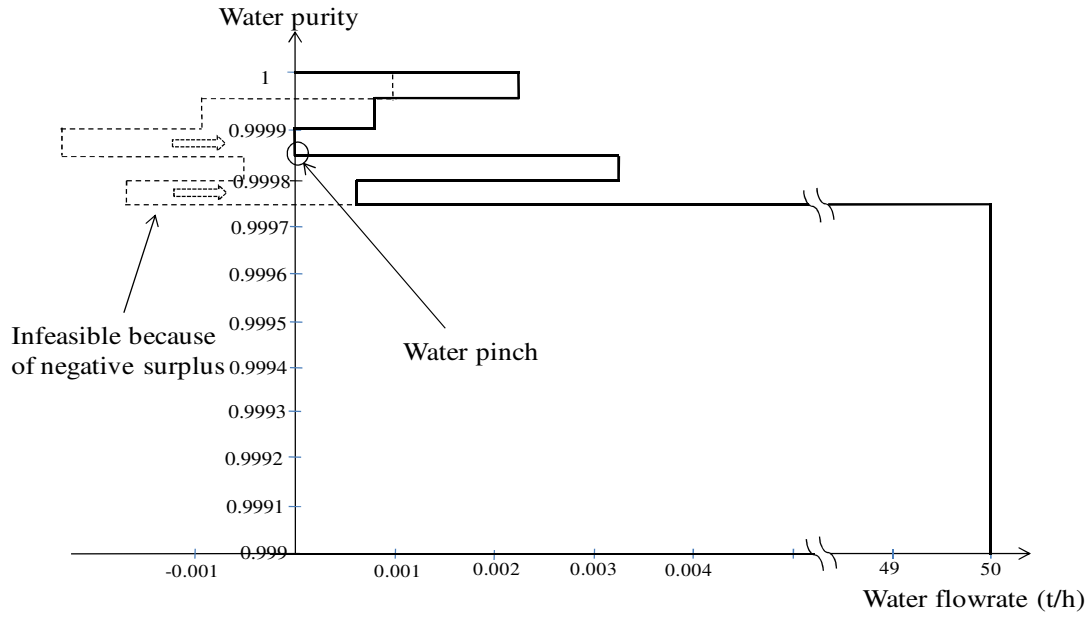


Figure 2 2: Water surplus diagram (Hallale, 2002)

The minimum freshwater target was obtained when the water surplus diagram just touched the vertical axis such that no part of the curve existed to the left of the vertical axis. This was achieved by guessing initial freshwater flowrates and thus modifying the source composite curve. In situations where some part of the surplus diagram existed to the left of the vertical axis, more freshwater had to be assumed. In situations where the surplus diagram existed too far to the right of the vertical axis, the guessed freshwater flowrate had to be reduced. Although the method gave true targets, the procedure of guessing freshwater flowrates and transferring data from one diagram to the other was cumbersome.

To overcome the limitations of Hallale (2002), Manan *et al.* (2004) developed a numerical technique called the water cascade analysis, WCA, in which a water cascade table, WCT, was used for flowrate targeting. In summary, the table consisted of nine columns. The concentration levels in a problem (C_k) were arranged in ascending order. The intervals, ($k = 1, 2, \dots, n$) were located in column 1 and the corresponding concentrations in column 2. In columns 3 and 4, the flowrates of water sinks, (F_j) and water sources, (F_i) were placed in their respective concentration levels. In column 5, the net flowrate, $\left(\sum_i F_i - \sum_j F_j \right)_k$ in each interval was calculated. The net water flowrate was cascaded down the concentration

intervals to give the cumulative surplus/deficit flowrate, $(F_{C,k})$ in column 6, with an assumption of zero freshwater flowrate. In column 7, the impurity load, (Δm_k) was calculated from the product of cumulative flowrate and the concentration difference across subsequent intervals, $(C_{k+1} - C_k)$. The impurity load was cascaded down the concentration intervals to give the cumulative impurity load, $(\text{cum}\Delta m_k)$ in column 8, which was equivalent to the water surplus diagram (Hallale, 2002). In column 9, the freshwater flowrate was calculated from Equation (2.1), where C_{FW} was the concentration of freshwater.

$$F_{FW,k} = \left(\frac{\text{cum}\Delta m_k}{C_k - C_{FW}} \right) \quad (2.1)$$

In column 9, the earlier assumed zero freshwater flowrate in column 6 was replaced by the absolute value of the largest negative $(F_{FW,k})$. This was in order to obtain a feasible cascade. This value, was the minimum freshwater flowrate, (F_{FW}) . The final row in column 6 was the wastewater flowrate, (F_{WW}) . The pinch was located at the concentration where $(\text{cum}\Delta m_k)$ was zero. This method did not involve any iteration. The works by Hallale (2002) and Manan *et al.* (2004) were only focused on flowrate targeting and not network synthesis.

Agrawal and Shenoy (2006) addressed the problem of obtaining the minimum freshwater flowrate for fixed flowrate problems. In this work, the fixed flowrate problem was recast into an equivalent fixed load problem to allow a limiting composite curve to be plotted. Similar to the method by Wang and Smith (1994) for fixed load problems, a water supply line was drawn such that it touched the limiting composite curve. The reciprocal of the slope of this line was the minimum freshwater flowrate. Agrawal and Shenoy (2006) observed that the recasting of data and the subsequent graphical application could be complicated. Hence, they proposed a numerical procedure called the composite table algorithm, CTA. The method gave absolute targets, reduced computation and was non-iterative. The CTA was conceptually the same as the WCA developed by Manan *et al.* (2004). To synthesize the network equivalent to the obtained targets, an algorithm based on the principle of nearest neighbours developed by Prakash and Shenoy (2006) was employed. This principle stated that the sources selected to

satisfy a particular water demand must be the nearest available neighbours with respect to contaminant concentration.

Up to this point, the water networks have been synthesized after the water targets were obtained. This is not the case with the water sources diagram, WSD, by Gomes *et al.* (2007) for fixed load problems. The WSD is a diagram where each stream is located in its appropriate concentration level from left to right. Next, the mass load of each operation is calculated in each concentration interval. Once the mass loads are obtained, the water network is synthesized by following specific rules about source to sink allocation. Herein lies the difference, the WSD is an interactive technique where the network is synthesized as the calculations are performed, the targets are not obtained beforehand. The selling point of their method was that it could be used by process engineers to calculate problems by hand. The method as presented would be difficult to apply to large scale problems as the solution would become more complex.

The methods discussed so far have employed graphical/numerical techniques for addressing wastewater minimization in continuous processes. Graphical techniques are inadequate in their ability to cater for constraints other than concentration and flowrate. In addition, these methods are usually limited to single contaminants. Consequently, mathematical techniques have been adopted. The problem with mathematical techniques is in ensuring global optimality. In situations where the mathematical model is linear, the solution obtained can be guaranteed to be the global solution. Wherever it is possible to linearize a model, this is preferred. However, nonlinearities in models are often unavoidable. The manner in which some authors address this problem is discussed.

2.2 Mathematical techniques for wastewater minimization in continuous processes

Bagajewicz and Savelski (2001) addressed single contaminant problems using a linear mathematical formulation. In the formulation, water and contaminant balances were performed for each water-using process. The linearity of the model was due to the fact that the inlet and outlet contaminant concentrations were assumed to be at maximum. Consequently, bilinearities that existed when concentration was multiplied with another

variable e.g. flowrate, were eliminated. This work also investigated different network alternatives associated with different objective functions, such as minimum number of connections between units, minimum fixed cost, where cost was defined in terms of piping costs and the elimination of forbidden or enforcement of compulsory matches.

The mathematical technique by Doyle and Smith (1997) addressed multiple contaminants. To address the problem of varying water requirements by different contaminants, Equation (2.2) was solved for each contaminant present in the problem. The limiting flowrate, F_{lim} was defined as the maximum flowrate across all contaminants. At this limiting flowrate, at least one of the contaminants reaches its maximum outlet concentration.

$$F_{lim} = \frac{\Delta m}{C_{out,MAX} - C_{in,MAX}} \quad (2.2)$$

The mathematical optimization was based on a superstructure, where the inlet of every operation was connected to the outlet of every operation and to each freshwater source. Three scenarios were considered in this study. In the first scenario, water-using operations that could be modeled as fixed load problems were considered. In this scenario, it could not be assumed that all the contaminants were at their maximum, like was done for the single contaminant case by Bagajewicz and Savelski (2001). The resulting model was a nonlinear program, NLP due to the bilinearities that existed in the contaminant mass balances around each operation, when concentration was multiplied with flowrate. In the second scenario, water-using operations that could be modeled by a fixed outlet concentration (contaminants were assumed to go to their maximum solubility) were addressed. Here, the resulting model was a linear problem, LP. The third scenario considered both types of water-using operations in one problem. This resulted in a NLP. To address the nonlinearity of the problem, it was proposed to use the solution from a linear model, where concentrations were assumed to be at their maximum to provide an initialization for the nonlinear optimization. The objective function was the minimization of freshwater cost, where cost was directly proportional to flowrate. The model could easily accommodate situations where there were flow losses or flow gains.

Huang *et al.* (1999) adopted a similar initialization approach to address the nonlinearities in their NLP model for minimizing the rate of freshwater consumption. The equality constraints of the NLP model were solved by fixing the extra degree of freedom with reasonable guesses of the key design variables. These guesses were obtained from the stream data of a base case flowsheet which was available. In addition, it was stated that in some cases, certain operations were better modeled as having fixed outlet concentrations instead of as fixed load or fixed flowrate operations. The review paper by Bagajewicz (2000) discusses mathematical techniques adopted for wastewater minimization in continuous processes in more detail.

In compliance with environmental legislation, wastewater must be treated before it is discharged to the environment. This is simply end of pipe treatment. On the other hand, wastewater regeneration has been widely accepted as an effective means to increase wastewater minimization and is usually employed after the opportunities for wastewater reduction via water reuse/recycle have been exhausted. Wastewater treatment/regeneration in industry usually occurs in multiple stages, however in literature, it is often modeled using one stage. Multiple treatment units have also been considered. Regardless of whether wastewater treatment or regeneration is considered, the pertinent issues are:

- determining the minimum flowrate of the regenerator/treatment unit and
- the identification of streams to be treated

In addition, the type of regenerator/treatment unit employed plays a role in the way the problem is addressed. Two types of regenerators/treatment units are considered in literature:

- Regenerator with a fixed outlet concentration. Here, the concentration of wastewater is reduced to this value regardless of the quality of the inlet water. Examples of this are filtration, membrane separation, centrifugal separation and biological treatment.
- Removal ratio type regenerator. In this case, a fraction of the impurity load is removed depending on the concentration of the inlet stream. Examples are scrubbing, stripping, extraction and evaporation. The mathematical expression for this is given in Equation (2.3)

$$RR = \frac{f_{in}C_{in} - f_{out}C_{out}}{f_{in}C_{in}} \quad (2.3)$$

2.3 Regenerator flowrate determination

According to McLaughlin *et al.* (1992), capital and operating costs of most wastewater treatment processes are proportional to the total flowrate of wastewater which flows through the treatment process. Hence the treatment of large volumes of wastewater is expensive.

Kuo and Smith (1997) addressed this problem with a distributed effluent treatment system as opposed to a centralized treatment unit. The distributed system utilizes multiple treatment units to segregate effluent streams for treatment and only combine them when necessary. A graphical method based on the limiting composite curve was used. To apply the method, it was required to know beforehand the flowrates and concentrations of the wastewater streams, the available treatment processes and their corresponding removal ratios and the environmental discharge limit. In this way, instead of the usual limiting composite curve, a composite effluent curve was plotted. Similarly instead of a water supply line, water treatment lines (each line corresponding to a treatment unit) were drawn against the effluent composite curve. The reciprocal of the slopes of the treatment lines gave the flowrate through the treatment units. In the presence of multiple treatment units, the determination of the best order of treatment was not a trivial task, hence Kuo and Smith (1997) proposed an approach based on exergy analysis to evaluate wastewater degradation encountered from the various treatment schemes possible. The drawbacks of the method were that the effluent treatment network was considered in isolation from the water-using operations and the composite curve method was tedious in its application to multiple contaminants. To synthesize the corresponding network, the design rules of Wang and Smith (1994) were followed. Streams starting above the pinch for the treatment system were treated fully, those starting at the pinch were treated partially and partially bypassed treatment and those starting below the pinch completely bypassed treatment.

Kuo and Smith (1998) rightly pointed out that many researchers considered on an individual basis, the water-using operations, treatment system and the regeneration system instead of

investigating the interactions between all three. Figure 2.3 is an illustration of the total water network, within which the individual elements interact with each other.

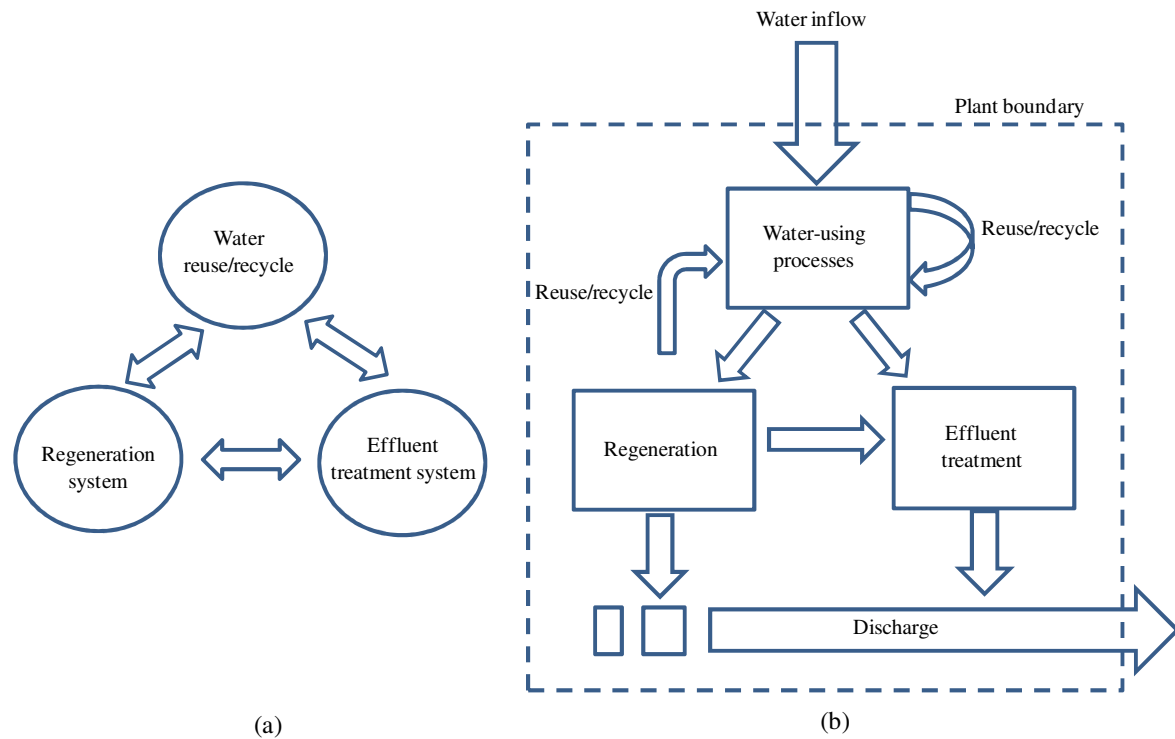


Figure 2.3: (a) Systems in isolation (b) Interactions between elements of the water system (Kuo and Smith, 1998)

Agrawal and Shenoy (2006) considered regeneration as opposed to wastewater treatment. A central regenerator based on a fixed outlet concentration was used. In their method water reuse among the water-using operations and regeneration were considered within the same framework. This is Figure 2.3(b) without effluent treatment. The method also utilized the graphical limiting composite curve. Here, the limiting composite curve was plotted as already discussed above. The difference was that the water supply line was a combination of freshwater and regenerated water to achieve the minimum freshwater target. The draw back of this method as pointed out in the review by Foo (2009) was that when the limiting composite curve had a turning point near the composite water supply line, the freshwater flowrate had to be increased.

None of the approaches discussed so far could guarantee the determination of the minimum regeneration flowrate along with the minimum freshwater and wastewater flowrates. Ng *et al.* (2007a) and Ng *et al.* (2008) proposed a procedure to determine the ultimate water targets for a given regeneration outlet concentration. The method was applicable to both fixed flowrate and fixed load problems. The regeneration targeting procedure was as follows. The first step was the allocation of all water sources and sinks into two regions, i.e., freshwater and regeneration regions. The freshwater region, FWR, could receive water from both freshwater and regenerated water, while the regeneration region, RWR, could only receive regenerated water. In the FWR, sources and sinks with concentrations lower than the given regenerator outlet concentration were allocated while sources and sinks with concentrations higher than the regenerator outlet concentration were allocated to the RWR. The next step, called reallocation, was to ensure that the total sink water flowrate equalled the total source water flowrate in the RWR. To do this, certain heuristics were stipulated to handle the two scenarios that could be encountered, which were a scenario where the total source flowrate was higher than the total sink flowrate and vice versa. After the reallocation was completed, a water cascade analysis was performed on both the FWR and the RWR. The freshwater and wastewater targets were obtained from the FWR, while the minimum regeneration flowrate was targeted by the RWR. These were termed the ultimate flowrate targets which were the lowest possible freshwater, wastewater and regenerator flowrates after reuse/recycle had been maximized among all the water using processes.

Huang *et al.* (1999) used a mathematical optimization method to determine the minimum wastewater treatment capacity in multiple contaminant problems. In addition to the mass and contaminant balances around each water-using operation, water and contaminant balances were performed around the treatment unit. Water loss in the treatment unit was considered, whereby the water loss was modeled as being proportional to the water flowrate into the unit. This is characteristic of filtration, membrane separation and evaporation. To address multiple contaminants, multiple treatment units were considered, one for each contaminant. The two different types of regenerators were also investigated, i.e. constant removal ratio type regenerator and fixed outlet concentration type. The objective function was the minimization of the costs associated with running the water-using operations and the water treatment units. Each cost term was roughly proportional to the flowrate through the unit. The resulting model was a NLP for which a method of initialization was proposed as aforementioned.

In the mathematical model by Bagajewicz and Savelski (2001) involving a single contaminant, one regenerator of the fixed outlet concentration type was considered to be present. This led to a linear model. In order to minimize the amount of water sent through the treatment process, they showed mathematically that this would be achieved if the outlet concentration from the regenerator was as small as possible. Firstly the mathematical model involving water-using operations and regeneration determined the minimum freshwater target, F . The objective function in this step was the minimization of total freshwater usage in each unit, F_j^w . This is given in Equation (2.4)

$$\text{Min} \sum_j F_j^w = F \quad (2.4)$$

Secondly, the minimum water flowrate through the regenerator was obtained by minimizing the total water flow from unit to regenerator, $F_{j,T}$ such that the total amount of freshwater used in the water-using units amounted to the target F obtained previously. This is given in Equation (2.5).

$$\text{Min} \sum_j F_{j,T} = \text{minimize wastewater flowrate, such that } \sum_j F_j^w = F \quad (2.5)$$

Bandyopadhyay (2009) developed a method to target the minimum waste treatment flowrate. Only one treatment unit was considered. The method which was restricted to a single contaminant was a combination of algebraic analysis using table calculations and a graphical representation (cumulative contaminant load vs. concentration called the waste composite curve). The table calculations were similar to the water cascade table by Manan *et al.* (2004). At the end, the minimum waste flowrate to the treatment unit was determined. The method incorporated water losses in the regenerator. The flow loss was assumed proportional to the inlet flowrate to the treatment unit.

Ulson de Souza *et al.* (2009) utilized the WSD developed by Gomes *et al.* (2007) to reduce treated water consumption, where multiple contaminants were present. The performance of the regenerator was given in terms of maximum outlet concentration. Multiple treatment units were utilized for the removal of the different contaminants. The method was an algorithmic

procedure based on heuristics and considered reuse/recycle, treatment and regeneration within the same framework, as illustrated in Figure 2.3(b).

2.4 Appropriate regenerator placement

The streams selected to be regenerated have an effect on the impurity load that will be removed by the regenerator. As aforementioned, this will affect the cost of the treatment system. In the work by Wang and Smith (1994), the inlet to the regenerator consisted of water streams that had reached the pinch concentration after they had been recycled/reused. This was similarly applied by Agrawal and Shenoy (2006) but for fixed flowrate problems. Foo (2009) observed that this approach of regenerating water at the pinch concentration may fail to locate the minimum water targets in cases where the pinch is reallocated to a new concentration after regeneration has taken place.

Hallale (2002) was guided by the water surplus diagram in placing regenerators with a fixed outlet concentration. In this work it was determined that regeneration units should be placed across the pinch concentration, whereby water to be regenerated is drawn from regions having concentrations higher than the pinch (with excess water) to regions having lower concentration than the pinch (with water deficit). This is due to the fact that water is taken from a region of surplus and returned to a region deficient of pure water. This led to the biggest savings in both freshwater and wastewater when compared to the placement of the regenerator above or below the water pinch.

Ng *et al.* (2007b) utilized the water cascade analysis developed by Manan *et al.* (2004) for flowrate targeting and the minimum regeneration flowrate targeting method by Ng *et al.* (2007a) to identify the water streams to be regenerated. The regeneration targeting model was based on the assumption of a fixed outlet concentration from the regenerator. Once the pinch causing source was identified from the WCA, the water sources and sinks were segregated into lower and higher concentration regions. The wastewater from the pinch source was regenerated first. This is due to the fact that it is the cleanest of all the wastewater streams. In cases where the flowrate of the pinch waste stream was lower than the minimum regeneration flowrate (the water was not sufficient), the wastewater stream(s) of the next higher concentration was/were sent for regeneration. This was continued until the regeneration

flowrate target was fulfilled or until all wastewater streams were regenerated. A corresponding graphical method for waste stream identification was also demonstrated in their work.

2.5 Advancements in the wastewater minimization problem

The work by Lim and Park (2008, 2009) used mathematical optimization to address the synthesis of the most environmentally friendly wastewater treatment network. In their work, a terminal treatment plant was included in the distributed water treatment system to ensure that discharged wastewater consistently met stipulated limits. This new system was termed the total wastewater treatment network system, TWTNS. A life cycle analysis was performed to evaluate the environmental impacts of certain principal contributors. The principal contributors investigated were limited to piping in the construction stage, electricity for pumping and wastewater treatment in the operation and maintenance stage and recycling of pipelines in the disposal stage. In order to incorporate the life cycle analysis into the model mathematically, the results obtained from documented life cycle analysis, LCA, standards were fitted to generate linear regression equations of the environmental impact of the contributors. For example, the LCA results of piping were used to generate a linear regression equation which enabled the prediction of the environmental impact of a pipeline with a given cross sectional area and length. Two objective functions were considered. The first objective function was the minimization of the total environmental effects over the life cycle of the plant. The second objective function was the minimization of the total flowrate of treated wastewater. The model resulted in a MINLP problem for which the solution could not be guaranteed to be globally optimal. A model of this nature could become very large and complex, hence, a choice of what aspects of the plant to focus on had to be made. In addition, assumptions in various relationships/equations were made in order to simplify the model.

Ng *et al.* (2009) developed an automated targeting method to synthesize a total property-based network. In the past, waste streams have been identified by contaminant concentration. In property-based methods, waste streams are classified in terms of properties such as pH, turbidity, hardness, toxicity, colour, density, reflectivity, relative volatility, etc. This is due to the fact that certain processes are better described using properties rather than contaminant concentration (El-Halwagi *et al.*, 2004). The method by Ng *et al.* (2009) has the advantages

of both insight based (the various network targets are obtained prior to synthesis) and mathematical optimization approaches. The aim was to synthesize simultaneously a total network that included material reuse/recycle, regeneration/interception and waste treatment (see Figure 2.3). In property-based methods, property is treated in an analogous manner to contaminant concentration. A linearized property mixing rule is adopted to define all possible mixing patterns among individual properties of streams. The mixing rule is of the form in Equation (2.6)

$$\psi(\bar{p}) = \sum_i x_i \psi(p_i) \quad (2.6)$$

where $\psi(\bar{p})$ and $\psi(p_i)$ are linearizing operators on mixture property $\bar{p}$ and stream property p_i , respectively. x_i is the fractional contribution of stream i in the total mixture flowrate. The work by Ng *et al.* (2009) was applicable to single properties. The drawbacks of the method are as follows. Firstly, it is well known that property mixing rules can be very nonlinear, linearizing of which becomes difficult. Secondly, the accuracy of such property mixing rules cannot be guaranteed. Using an incorrect property rule will lead to errors and will prevent any method based on them to be practical in their use.

The methodologies developed for wastewater minimization in continuous processes have provided many insights, namely the pinch point. However, the aforementioned techniques cannot readily be applied to batch processes without some necessary modifications. Consider the illustration in Figure 2.4, a water-using batch process is characterized not only by flowrate and concentration but also by time. This is in contrast to a continuous process which is characterized by flowrate and concentration only. As can be observed from Figure 2.4, for the continuous processes, water from process A can be reused in process B because the concentration requirement is met. Water from B cannot, however, be reused in A because it is too contaminated. On the other hand for the batch processes, water from A can be reused in B if process A ends before process B begins. This constraint is in addition to the concentration requirement. Water from B cannot be reused in A because it is too contaminated and also because it takes place after process A.

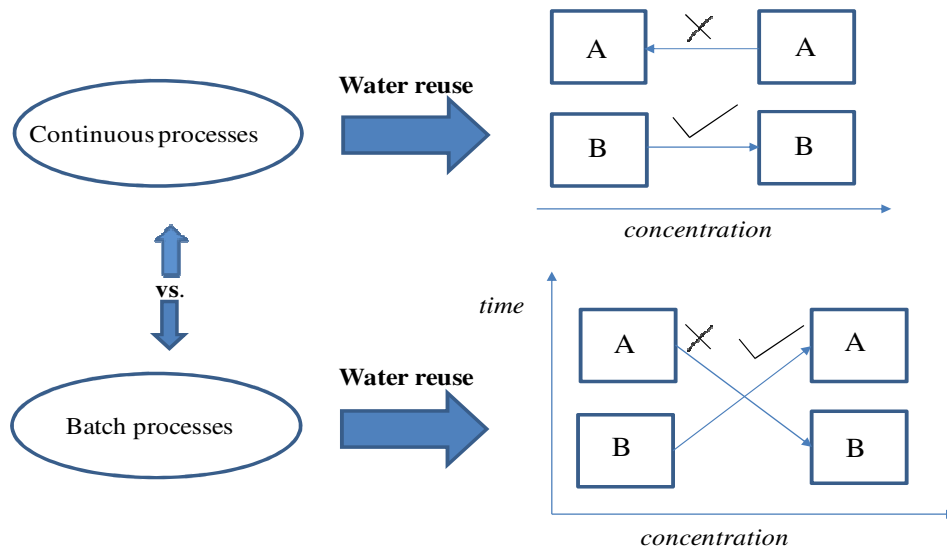


Figure 2.4: Comparison between batch and continuous processes

For this reason in batch processes, the requirement for water is time dependent, hence, time must be addressed in conjunction with the wastewater minimization problem. In order to override the time constraint and maximize water reuse even further, wastewater storage has been employed in literature, called indirect reuse. This is as opposed to direct reuse which is water transfer from process to process provided the time at which water is available coincides with the time at which water is required. Below is a discussion of wastewater minimization methodologies in batch processes.

2.6 Graphical/numerical techniques for wastewater minimization in batch processes

A characteristic of these methods is that information about the starting and finishing times of the water-using batch operations is essential to solve wastewater minimization problems. In general, to address both concentration and time constraints, these methods require two dimensions over which the calculations are performed. For instance, when concentration is considered as the primary constraint and time as the secondary constraint, water is cascaded in one concentration interval through all the time intervals before water is cascaded to the next concentration interval and so on. In this way, water of a lower concentration is reused in later time intervals and for operations with a higher concentration requirement. This was the procedure followed by Wang and Smith (1995) who extended their work for continuous

processes (Wang and Smith, 1994) to batch processes. The problem was divided into concentration intervals and time subintervals with the boundaries of the intervals determined by the endpoints of the individual processes. Targeting was performed in each concentration interval by reusing water which was available in its own time subinterval, where possible. Any surplus water could be reused in subsequent time intervals in the same concentration interval or could be stored for reuse in later concentration intervals. When no opportunities for recycle/reuse existed, freshwater was used. The overall freshwater target was the accumulated freshwater makeup required by the system and the eventual surplus was the total effluent of the system. This method permitted water reuse between units that were still in operation (operations with overlapping time intervals). This is possible for processes operating in a semicontinuous mode but not possible for strictly batch operations where water is available from a unit only at the end of its operation and water can be transferred to a unit only at the beginning of its operation. No systematic method was developed for the design of the corresponding batch network. Network design was done using insights drawn during targeting.

Majozi *et al.* (2006) modified the technique by Wang and Smith (1995) to address strictly batch processes. Two scenarios were considered to determine the effect of the targeting procedure on the final design. In the first scenario, time was treated as the primary constraint and concentration as the secondary constraint while in the second scenario, the primary constraint was concentration and the secondary constraint was time. The procedure for targeting in the first scenario was similar to the method by Wang and Smith (1995). In the second scenario, the problem was divided into time intervals and concentration subintervals. Targeting was performed in each time interval. Whenever possible any surplus water was transferred to higher concentration subintervals in the same time interval for reuse, or stored for reuse in later time intervals. In addition, surplus water could not be reused in lower concentration subintervals or previous time intervals. Any shortfall within any concentration subinterval could be made up from lower concentration subintervals, from previous time intervals or from freshwater. Similar to the previous case, the eventual surplus became the system effluent and the accumulated freshwater make-up constituted the system intake. At the end of their analysis, they found that reversing the priority of time and concentration constraints did not have any effect on the water target. The choice of which constraint to use could be based on the ease with which the targeting could be performed. The methods by Wang and Smith (1995) and Majozi *et al.* (2006) were applicable to fixed load problems.

Foo *et al.* (2005) presented a numerical technique based on pinch analysis that was applicable to fixed flow problems. In the context of batch processes, fixed flow corresponds to a fixed quantity of water needed or produced by water-using operations. The water cascade analysis (WCA) which was developed for continuous processes (Manan *et al.*, 2004) was utilized to determine water targets in batch processes. The method was carried out in two stages. In the first stage, the targeting stage, a method known as the time-dependent water cascade analysis was developed to identify the minimum water flows in a batch process. Typically, time was divided into time intervals where water demand and water sources could be found. The water sources and sinks were then located at their respective impurity concentration levels within the time interval in which they existed. Targeting was done in the time intervals using the water cascade analysis to obtain the minimum freshwater and wastewater flows. The overall freshwater and wastewater targets were obtained by summing the individual targets of all the time intervals. The second stage involved synthesizing the batch network that achieved the determined targets. Network synthesis was carried out independently for each time interval using the guidelines stipulated by Hallale (2002) and some feasibility constraints. Afterwards, the overall network called the time-water network diagram was developed using information from the sub-networks of each time interval. In the time-water network diagram, the interaction between the water demands/sources and time was shown. The methodology by Foo *et al.* (2005) was also applicable in the presence of a storage tank. The storage capacity, defined as the maximum amount of water that was sent to the storage tank was determined. In their method, the number of storage tanks was equal to the number of water sources at different concentration levels that were intended for reuse as a result of the fact that mixing of water sources of different concentrations was not allowed. They noted this as a potential pitfall of their method, whereby once the number of water sources for reuse increased, the complexity of the network increased.

Chen and Lee (2008) introduced a batch network design technique using a graphical representation called the quantity-time diagram, which allowed connections between sources and demands to be visualized. In this way, the utility consumption and network structure were determined simultaneously. Completely batch and semi-continuous processes modeled as fixed flowrate problems could be handled by this method. On the quantity-time diagram, the time axis guided the designer in ensuring that water sinks were satisfied with water sources that existed earlier in time, whereas the quantity axis indicated the total water flow needed or produced. To enhance water recovery, a source of lower concentration was used to

fulfill flow requirements of demands. Storage was also considered to enhance water recovery. Care was taken when selecting water sources to be sent to the storage tank, this was done in such a way that the concentration of water in storage did not exceed the maximum allowable requirement of the main water users. The number of storage tanks could be reduced by sending reusable sources with similar concentrations to a storage tank. At the end of the network design, the optimality of the results was checked using any of the established targeting methods in literature. It was found that the design results by Chen and Lee (2008) agreed with the freshwater targets from pinch analysis. The drawback of their method was that it could require multiple iterations to determine the optimum design.

In general, graphical techniques are constrained to two dimensions hence; they cannot be used to solve problems with more than one contaminant effectively. It is important to note that the above graphical/numerical techniques required that the starting and finishing times of the water-using operations be defined. This means that the production schedule cannot be optimized. Once an operating schedule is given, the minimum water targets determined are unique to the schedule and so are not guaranteed to be the true minimum.

2.7 Mathematical optimization techniques for wastewater minimization in batch processes

Much of the research done on wastewater minimization in batch processes has been based on mathematical optimization techniques. This is due to the fact that mathematical techniques:

- afford the opportunity to optimize different objective functions,
- are useful for handling multiple contaminant systems,
- can easily accommodate special restrictions e.g. forbidden matches, restrictions on flowrates etc and
- are capable of handling in a simultaneous manner, wastewater minimization and scheduling issues.

Literature on wastewater minimization using mathematical optimization followed a trend. Firstly, simple wastewater minimization problems with direct reuse were considered, followed by the introduction of storage and then the consideration of wastewater treatment or

regeneration. To prevent duplicity, the methods which include regeneration or treatment will be discussed under that topic. Most mathematical formulations begin with a superstructure, whereby all water-using operations and their interactions with all other processes and equipment units are represented. According to Gouws *et al.* (2010) there are different ways of representing superstructures for batch problems. One way is to classify them based on the use of intermediate storage. Following this classification, when a storage tank is used to facilitate water reuse among water-using operations, it is referred to as indirect integration, as opposed to direct integration when no intermediate storage is present. Once the superstructure has been determined, water and contaminant mass balances are performed around every available water-using batch unit, storage tank and regenerator. Constraints associated with capacity, operation of the process and time dimension are also included. With regards to the handling of time, the methodologies for wastewater minimization in batch plants can be divided into two, namely:

- fixed schedule problems, where the starting and finishing times of the batch operations are known before optimization is performed, and
- variable schedule problems, where the starting and finishing times of the batch processes are optimization variables. The wastewater minimum and the corresponding batch schedule are determined after optimization.

The solution strategy in each methodology varies depending on how nonlinearities are addressed. These subject matters will be discussed.

2.7.1 Mathematical formulations based on a fixed schedule

The first batch water networks in literature were solved based on the assumption of the existence of an optimal batch schedule. These problems are simpler to solve than in the variable schedule case. Almato *et al.* (1997) developed a technique that utilized storage tanks to override the time constraint in the exploration of reuse and recycle opportunities. No direct reuse/recycle options were included in the superstructure hence, water recovery was only possible through storage vessels. The method was applicable to fixed load problems. The objective function considered was the minimization of freshwater use. The mathematical model resulted in a NLP. A two step procedure was used to obtain the solution of the model.

The first step involved heuristics to find the initial tank to stream assignment and to provide the NLP with a feasible starting solution. The second step was an optimization step to solve the NLP. The optimality of the solution could not be guaranteed.

Kim & Smith (2004) developed a MINLP which exploited water reuse and a storage facility to link different time periods. The superstructure included both direct and indirect integration. Direct water reuse could only occur between two operations taking place within the same time interval. Reuse of water between two operations in two different time intervals took place through storage. It is also imperative to note that water flow through a unit took place during the duration of that unit's operation. This is not strictly batch mode but rather semicontinuous. The method was based on the fixed load model for water-using batch processes and was applicable to multiple contaminant problems. The mass balances included water gains and losses. Water from operation to storage and vice versa was not explicitly taken into account in the mass balances. Instead a binary variable associated with the existence of a storage tank, Y_n^{ST} was defined. Similarly a binary variable associated with water reuse from operation n to operation n' , both representing water-using operations was defined. An extra constraint was formulated to describe the relationship between the two binary variables. This is given in Equation (2.7).

$$Y_{n,n'}^{PP} - Y_n^{ST} \leq 0 \quad \forall n, \text{ where } T_{n'}^S \geq T_n^E \quad (2.7)$$

The constraint states that if water is transferred from n to n' , i.e., $Y_{n,n'}^{PP} = 1$ where operation n' starts after operation n ends, then $Y_n^{ST} = 1$, i.e., a storage tank exists.

Constraints to limit the number of inlet and outlet streams for each operation and control compulsory or unacceptable matches were included. This was to reduce network complexity and improve its practicality. The objective function was the minimization of annual cost which consisted of the cost of freshwater, storage tank and piping. In terms of solution strategy, an MILP-LP decomposition of the original MINLP problem was proposed to find an initial solution for the MINLP. First, an MILP was obtained from the MINLP by fixing the outlet concentration, thus eliminating bilinear terms. The solution to the MILP identified connections between the various units and tanks. This information and the values of the

flowrates were then substituted into the original MINLP to give an LP. The LP problem was solved and the values of the concentrations determined were then used to update the MILP. The MILP and LP were iterated until the required convergence criteria were met. The output from this was then used as an initial solution for the MINLP. Due to the solution strategy, long solution times could result.

Majozi (2005a) developed a mathematical formulation which exploited recycle and reuse opportunities. The formulation considered a single contaminant and was based on a superstructure that included direct integration only. The time horizon was represented by a number of time points and each variable was defined at each time point. The formulation catered for truly batch operations. In doing so, water was used in a unit at time point p and produced at time point $p+1$. Sequencing constraints were included to ensure that water reuse coincided with the time it was available from the water source and the time it was required by the water sink. Two binary variables were required: $y(s_{out,j}, p)$ associated with the usage of a state for the mass balance and $y_r(s_{out,j}, s_{out,j'}, p)$ associated with reuse for the sequencing constraints. The relationship between the two binary variables is expressed in Equation (2.8).

$$y_r(s_{out,j}, s_{out,j'}, p) \leq y(s_{out,j'}, p) \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (2.8)$$

This equation simply states that for a unit j to transfer water to unit j' , unit j' should require water at that time point. It does not, however, mean that unit j' must use water from unit j , it could still obtain water from the freshwater source. State as employed in this work referred to the identity of a water stream. The objective function was the minimization of freshwater or effluent. The model resulted in a MINLP problem due to the bilinearities in the contaminant mass balances. The MINLP was linearized to a MILP by fixing the outlet concentrations and using the Glover transformation (Glover, 1975).

Shoaib *et al.* (2008) utilized a mathematical optimization technique requiring three stages for batch water network synthesis. The mass balances were based on the fixed flow model, so each batch process was modeled as a source and a sink. The superstructure was based on indirect integration. In the first stage, the objective was to determine the minimum freshwater usage. In the second stage, the minimum freshwater usage identified in the first stage was

included as an extra constraint. The objective was the minimization of storage tank capacity. The objective in the third stage was the minimization of the number of interconnections between the batch processes and the storage tanks. In this stage, the objective values from stages 1 and 2 were included as additional constraints. The overall model was an MINLP. The linear relaxation technique proposed by McCormick (1976) was adopted to relax the bilinear terms in the MINLP to form an MILP. The MILP was solved to produce an initial starting point for the exact MINLP. A key assumption made in this work was that only indirect water reuse was allowed i.e., the reuse of water between sources and sinks was done via a storage tank. This was to allow for proper mixing in the tanks so that the water reached the desired quality. The drawback of their method was that stored water could only be reused/recycled by sinks in the next batch cycle. Hence, the work was limited to cyclic operation.

As previously stated, the limitation of these methods is that they are based on the optimal schedule being given *a priori*. In practical terms, they are suited to situations where the batch schedule seldom changes.

2.7.2 Scheduling concepts to understand formulations based on variable schedules

Mathematical formulations based on variable schedules determine the minimum water flows, the corresponding batch water network together with the batch schedule. The unique feature of these formulations is that they are based on a scheduling framework.

Scheduling is at the heart of any problem facing batch processes. It is a decision making process to determine the appropriate time intervals within which certain tasks occur and to which units these tasks must be allocated, in order to maximize profits. In other words, a batch process schedule determines when, where and how to produce a set of products given a set of limited resources, the processing recipes and the specific time horizon (Ierapetritou and Floudas, 1998). Research on the scheduling problem in batch plants is very vast, with the aim of developing robust methodologies with short solution times. As the work in this dissertation was focused on wastewater minimization and not the development of new scheduling techniques, only the basic concepts necessary to understand scheduling in batch processes is presented. However, excellent review papers on the subject are: the works by Mendez *et al.* (2006) and Floudas and Lin (2004).

Two issues that are important in solving the scheduling problem are the time representation of events and flowsheet representation. These affect the quality of the mathematical model which is characterized by: the size of the model, number of binary variables and continuous variables, number of constraints, size of the integrality gaps and linear relaxation techniques. There are two main types of time representation, the discrete representation of time and the continuous time representation.

The discrete representation of time

In this instance, the time horizon is divided into a number of intervals of fixed length. The starting and finishing times of a task coincide with the boundaries of the interval. Too few time intervals lead to an inaccurate model which yields suboptimal results. To improve the accuracy of the model, the number of time intervals must be increased which leads to an increase in the overall size of the model because a binary variable is associated with each interval. An advantage of this representation is that the time grid is fixed and common for all equipment which makes the formulation simple and straightforward.

The continuous time representation

This is also referred to as the uneven discretization of time, whereby the starting or finishing time of a task is allowed to take place at any point in the time horizon. Unnecessary time intervals are eliminated and hence lead to a smaller model. The time horizon is discretized unevenly into time intervals. The time points coinciding with the starting or finishing of events are unknown beforehand and must be determined iteratively. The optimum number of time points is the one that gives the best objective value. Due to the variable nature of the timing of events, the modeling of a problem requires more constraints. This leads to a model with complicated formulations which could be difficult to solve.

With regards to the flowsheet representation, a given flowsheet could be represented by a network representation or a sequential representation. The network representation could be the state task network, STN, the resource task network, RTN or the state sequence network, SSN.

The state task network

The STN was developed by Kondili *et al.* (1993). This representation can describe accurately very complex production recipes involving mixing, splitting and recycling. Material balances associated with the processes are taken into account. The states are used to represent feeds, intermediates and final products and are denoted by circles. The tasks are operations which transform one state into another and are represented by rectangles. The arcs link the states to the tasks and denote the flow of material. A binary variable W_{ijt} is used to allocate tasks to units. It has a value of 1 if a task i starts in a unit j at time t . The number of binary variables associated with this representation is $i \times j \times t$.

Ierapetritou and Floudas (1998) decoupled the task events from the unit events in the STN. Two binary variables, $wv(i, t)$ and $yv(j, t)$ were used to define the beginning of a task and unit event respectively. The number of binary variables in this formulation was $(i \times j) + t$ which was less than $i \times j \times t$. This led to a smaller model. Their formulation also exploited the one to one relationship between units and tasks (a unit is allocated to a specific task) in a bid to decompose the problem to a smaller size. This decomposition was not possible in the absence of the one to one relationship.

The resource task network

Pantelides (1994) proposed the resource task network. The RTN is similar to the STN except that resources are also viewed as being produced and consumed like states. Examples of such resources are energy, manpower, transportation facilities and storage in addition to what were described as states under the STN, feed, intermediates and products. The RTN is useful in problems that involve identical equipment.

The state sequence network

The SSN was developed by Majozi and Zhu (2001). Only states are represented, thereby eliminating the need for task and unit binary variables as required by the STN representation. A task is implied between two different states. The states defined previously are represented by circles. The arc linking one state to another implies that a task has taken place and

represents the flow of material. A single binary $y(s, p)$ has a value of 1 if a state s is used at time point p . The total number of binary variables associated with this representation is $i \times t$ and is less than that proposed by Ierapetritou and Floudas (1998). When more than one state is used simultaneously in a unit, only one state is assigned the binary variable and is then termed the effective state, s^* . This formulation therefore leads to fewer binary variables compared with other approaches. No reduction in the number of binary variables is necessary as the correspondence between states, tasks and units is already taken into account.

The aforementioned network representation methods are effective at representing multipurpose plants. In multipurpose plants, each product can follow different equipment paths/processing sequence.

Sequential representation

This is a batch oriented representation suitable for describing flow shop processes found in multiproduct plants. In multiproduct plants, the products follow the same processing sequence. Multiproduct plants are a subset of multipurpose plants. Usually in the sequential representation, the splitting or mixing of streams is not encountered and so the consideration of mass balances is unnecessary. The resulting model size can be very large due to the fact that the number of sequencing variables depends on the number of batches to be scheduled. This method is not suitable for multipurpose plants.

General scheduling framework

The concepts mentioned above have been utilized in various combinations to develop scheduling formulations for batch processes. In general, these formulations consist of the following constraints:

- Allocation constraints, to ensure that only one task is performed in a unit at a time,
- Capacity constraints, which ensure that each piece of equipment is used within its maximum and minimum capacities,
- Material balance constraints, to ensure the conservation of mass,

- Sequence constraints, to ensure the right sequence of tasks in units that can perform more than one task,
- Duration constraints, which account for time spent in a batch unit and
- Objective function, which is usually the maximization of profit.

2.7.3 Mathematical formulations based on a variable schedule

These formulations are advantageous because they can easily accommodate the situation where the schedule is known and still determine the corresponding minimum water flow/cost solution. The most attractive of these formulations are those based on scheduling methodologies which are easy to solve and do not require long solution times.

Majozi (2005b) improved on his earlier formulation (Majozi, 2005a) by including the effect of central storage in the formulation and using a flexible schedule. Mass balances over the storage vessel were included as well as the sequencing constraints involving storage. Two additional binary variables, $y_{sin}(s_{out,j}, p)$ associated with transfer of water to storage and $y_{sout}(s_{out,j}, p)$ associated with transfer of water from storage were introduced. The scheduling framework of Majozi and Zhu (2001) that utilized the SSN and continuous time representation was employed. Four scenarios were investigated in the work by Majozi (2005b). In the first scenario, which was exactly the same as the work done in Majozi (2005a), it was assumed that the outlet concentration from each unit was fixed at its maximum value. This implied that during optimization, the flowrate through each unit was free to vary below a defined upper limit. This resulted in a MILP. The second scenario assumed that the flowrate through each unit was fixed, and the inlet and outlet concentrations were free to vary within defined maximum values during optimization. The third scenario was the same as scenario one but with a central reusable storage vessel included in the formulation. Likewise, the fourth scenario was the same as scenario two but with the inclusion of a central reusable storage vessel. Scenarios two, three and four resulted in MINLP problems for which global optimal solutions could not be guaranteed. The superstructures for scenarios three and four were also similar to that of Majozi (2005a), except that integration with storage was included. The superstructure for scenarios three and four is illustrated in Figure 2.5.

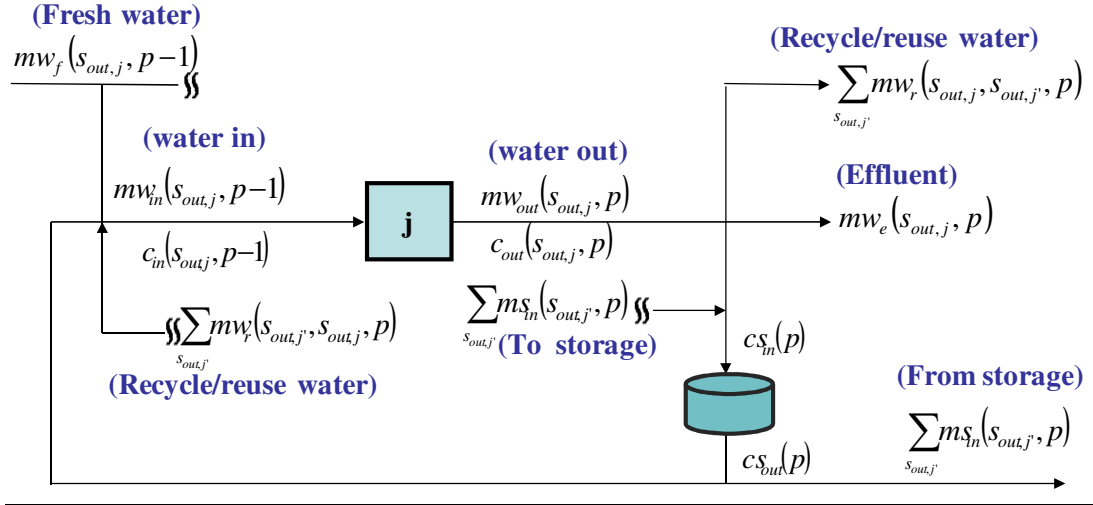


Figure 2.5: Superstructure of Majozi (2005b) for scenarios three and four

The method by Majozi (2005b) differs from other methods, in that, reuse could either be direct or indirect as opposed to the methods of Almato *et al.* (1997) and Shoaib *et al.* (2008), whereby reuse could only take place through a vessel. The limitation of the work by Majozi (2005b) was that it was limited to a single contaminant.

Gouws and Majozi (2008) addressed multiple contaminants and highlighted the fact that the choice of storage option depended on the profile of contaminants present in the water streams. Different wastewater streams could contain single but different contaminants. In another situation, each wastewater stream could contain the same set of contaminants. Yet another option could be a mixture of both cases, that is, there are wastewater streams with single but different contaminants as well as wastewater streams with multiple contaminants. The effect of multiple storage vessels and multiple contaminants is shown in Equation (2.9), which is an inlet contaminant balance into a unit. In this constraint, $c_{in}(j, c, p)$ is the inlet concentration into unit j of contaminant c at time point p , $f_u(j, p)$ is the amount of water into unit j at time point p , $f_r(j', j, p)$ is the amount of water recycled between unit j' and unit j at time point p , $c_{out}(j', c, p)$ is the outlet concentration of the water from unit j' of contaminant c at time point p , $fs_{out}(u, j, p)$ is the amount of water going into unit j from storage vessel u at time point p and $cs_{out}(u, c, p)$ is the concentration of contaminant c of water inside a storage tank u at time point p .

$$c_{in}(j, c, p)f_u(j, p) = \sum_{j'} f_r(j', j, p)c_{out}(j', c, p) + \sum_u fs_{out}(u, j, p)cs_{out}(u, c, p) \quad (2.9)$$

$$\forall j, j' \in J, p \in P, c \in C$$

Due to the bilinear terms in this equation, the overall model was nonlinear and nonconvex, hence the failure to ascertain global optimality. To reduce computational intensity, some of these nonlinearities were linearized using the reformulation–linearization method proposed by Quesada and Grossmann (1995).

Majozi and Gouws (2009) presented a mathematical formulation for wastewater minimization that included multiple contaminants with one central storage tank. Equation (2.10) is an inlet contaminant balance into a unit in this work. It is very similar to Equation (2.9) except for a few differences.

$$c_{in}(j, c, p)f_u(j, p) = \sum_{j'} f_r(j', j, p)c_{out}(j', c, p) + fs_{out}(j, p)cs_{out}(c, p) \quad (2.10)$$

$$\forall j, j' \in J, p \in P, c \in C$$

In this constraint, $fs_{out}(j, p)$ is the amount of water going into unit j from the central storage vessel at time point p and $cs_{out}(c, p)$ is the concentration of contaminant c of water inside the central storage tank at time point p .

2.8 Incorporating regeneration

Wastewater treatment and regeneration in batch plants have been considered in literature. The difference between treatment and regeneration was discussed under continuous processes.

Chang and Li (2006) investigated the concept of wastewater treatment, whereby buffer tanks were utilized to achieve wastewater flowrate and contaminant concentration equalization. The mathematical formulation was based on a superstructure which followed a number of rules. A splitting node was placed at the exit of each batch process and buffer tank, while a mixing node was placed at the entrance of each buffer tank and sink. Each splitting node after a batch process was connected to all mixing nodes in the superstructure, while each splitting

node after each tank was connected to all mixing nodes except the one at the entrance of the same tank. In this work, the sink was a treatment unit and only batch processes that generated wastewater were considered. The treatment unit was modeled as a continuous operation, hence, the need for buffer tanks. The mathematical formulation was based on a fixed schedule. In addition, the time horizon was discretized. This was in order to express differential equations as algebraic equations which were much easier to handle. The differential equations were encountered when performing water and contaminant mass balances around the buffer tanks. A disadvantage of the discretized time horizon as already mentioned is the explosive binary dimension that could be encountered in more complex problems leading to increased computational time. The objective function was the minimization of the installed cost of buffer tanks, given in Equation (2.11).

$$obj = \sum_{t \in T} \alpha (V_t^{max})^{0.6} \quad (2.11)$$

where α is a constant and V_t is the volume of a buffer tank. Worthy of mention is the fact that in this work the treated wastewater was not reused in the batch processes.

Li and Chang (2006) improved upon their earlier paper by considering water reuse between the batch processes. In this work, a batch process could be a source (water generating), sink (water consuming) or a water user (both water consuming and water generating). The superstructure was similar to Chang and Li (2006) but adjusted to account for the fact that a sink could consist of a treatment unit, the environment or a batch process. In addition, the mathematical formulation was based on a fixed schedule and a discretized time horizon. Their method was applicable to multiple contaminant systems. Water and contaminant mass balances were carried out at each splitting and mixing node, around each source, sink, water user and buffer tank. The contaminant mass balances at each node were carried out for each pollution index. The water balance over a buffer tank is given in Equation (2.12). In Equation (2.12), $v_{b,t}$ is the volume of water in buffer tank b at the end of time interval t , $f_{b,t}^{in}$ and $f_{b,t}^{out}$ are the inlet and outlet flowrates of buffer tank b during time interval t , respectively, and DT is the length of the time interval. Equation (2.13) is the contaminant balance over the same buffer tank. In Equation (2.13), $c_{b,k,t}^{in}$ and $c_{b,k,t}^{out}$ are the values of pollution index k in the input and output streams of buffer tank b at the end of time interval t , respectively.

$$v_{b,t} = v_{b,t-1} + (f_{b,t}^{in} - f_{b,t}^{out})DT \quad b \in B, k \in K, t \in T \quad (2.12)$$

$$v_{b,t} c_{b,k,t}^{out} \cong v_{b,t-1} c_{b,k,t-1}^{out} + (f_{b,t}^{in} c_{b,k,t}^{in} - f_{b,t}^{out} c_{b,k,t}^{out})DT \quad b \in B, k \in K, t \in T \quad (2.13)$$

The aim of this work was to design an integrated water reuse and equalization system for batch processes. The objective function was the minimization of annualized cost which consisted of annual water costs, annualized installation costs and annual treatment costs. The mathematical formulation resulted in a MINLP. Similar to Chang and Li (2006), reuse of treated water in batch processes was not considered. The treatment unit only served as a sink for wastewater.

In the work by Cheng and Chang (2007), all three systems, i.e., optimization of batch schedules, water reuse system and wastewater treatment system were incorporated in the same model (the formulation was based on a variable schedule). This is illustrated in Figure 2.6. The model was divided into two modules, namely, the batch production module and the batch water network synthesis module. The objective function of the scheduling module, which was based on the scheduling framework by Lee *et al.* (2001), was given as the difference between the revenue from product and the cost of raw material. The scheduling formulation of Lee *et al.* (2001) was based on the discrete time formulation and the STN. The batch water network synthesis module was similar to that of Li and Chang (2006). To optimize the schedule and the batch water network simultaneously, Cheng and Chang (2007) assumed that the water consumed or generated in a batch process was proportional to the amount of material produced. The objective functions from the two modules were combined by subtracting the water recovery objective function from the scheduling objective function. Constraints associated with the network structure were also incorporated, such as, the reduction of the number of storage tanks and pipe connections. Treated wastewater was not reused in the water system but simply discharged to a water sink which in this case, was the environment.

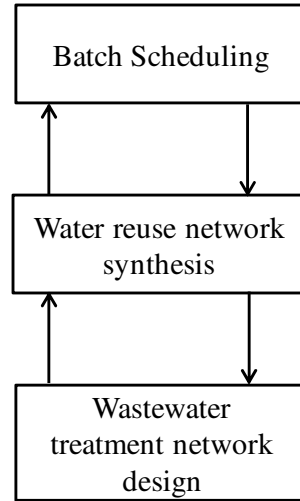


Figure 2.6: An integrated batch water network design (Cheng and Chang, 2007)

The use of a regenerator was considered in the work by Shoaib *et al.* (2008). To place the regenerator, the pinch concentration was firstly identified using the time dependent water cascade analysis TDWCA, already discussed under graphical techniques for batch processes. Once the pinch concentration had been located, the regenerator was placed across the pinch, i.e. the regenerator purified a water source at a higher concentration than the pinch concentration to a concentration lower than that of the pinch, as stipulated by Hallale (2002), this is the best option. The type of regenerator considered was the fixed outlet concentration regenerator. After the regenerator had been installed, stages 2 and 3 involving storage size and network complexity optimization respectively were carried out to synthesize the batch network. The freshwater used which is concomitant with wastewater generated, was decreased further compared to the situation where no regenerator was used.

Liu *et al.* (2009) considered the use of a central regenerator to explore more possibilities for water reuse and water recovery in batch plants. Similar to the work by Chang and Li (2006), the central regeneration unit operated continuously hence, storage tanks were installed at the inlet and outlet of the regeneration unit to act as buffers to connect the batch operations to the continuous regenerator. In their superstructure, the buffer tank at the entrance to the regenerator also served to provide indirect reuse water for the batch processes. In the mathematical formulation, the time horizon was discretized and was based on a fixed schedule. Equation (2.14) is the mass balance around the buffer tank at the entrance to the regenerator. In Equation (2.14), $Q_T^p(t)$ is the water remaining in tank T at any moment t ,

$Q_T^{p-1}(t_H)$ is the residual water in tank T at the end of the preceding operating cycle $P-1$, $Q_{T,j}^p(t)$ is the amount of water discharged from batch process j to tank T during operating cycle P , t^R is the start moment of regeneration and $f^{R,P}$ is the flowrate of the regeneration unit during operating cycle P .

$$Q_T^p(t) = Q_T^{p-1}(t_H) + \sum_{j \in J} Q_{T,j}^p u(t - t_j^{out}) - \sum_{j \in J} Q_{T,j}^p u(t - t_j^{in}) - f^{R,P}(t - t^R) u(t - t^R) \quad (2.14)$$

where

$$u(t) = \begin{cases} 1 & t \geq 0 \\ 0 & t < 0 \end{cases}$$

Two objectives were considered in this work, the first was the minimization of freshwater consumption and effluent generation of the system. The second was to minimize the flowrate of the regeneration unit. An advantage of their method was that they considered the need for a regenerator in a problem beforehand. This is because it is the nature of some problems, though unlikely in practice, that the wastewater produced by the batch processes is sufficient for use by the other processes on the plant. The regenerator becomes necessary in problems where wastewater generated is so highly contaminated that the water cannot be reused. However, this work was limited to single contaminant problems.

The method by Zhou *et al.* (2009) and Li *et al.* (2010) took into account batch production, the water-reuse subsystem and wastewater treatment (see Figure 2.6). The formulation was based on a variable schedule. In this work, the state-time-space superstructure was introduced, which identified states, tasks, equipment and time simultaneously. An illustration is provided in Figure 2.7. In spite of the exhaustive representation of the superstructure, the authors still found it necessary to exclude some connections made in the superstructure. The mathematical model consisted of two modules, the scheduling module and the batch water network synthesis module. The production scheduling framework was based on the MILP formulation proposed by Ierapetritou and Floudas (1998) which used the continuous time representation. The mathematical formulation for the batch water network was based on the discrete time formulation similar to that by Li and Chang (2007) with the exception that wastewater regeneration was incorporated. To link the two modules together, they assumed that the water generating or consuming rate in a water-using operation was directly proportional to the

processing volume of the batch unit in the batch module. Structural constraints to reduce the number of pipelines were also included in the model. The overall model was a nonconvex MINLP and was solved using a hybrid optimization strategy with iteration. The authors acknowledged the possibility of computational difficulties associated with a problem of this nature. The solution strategy decomposed the original MINLP into a MILP-MINLP formulation that was solved sequentially. The MILP model was the production formulation for scheduling. The solutions from this stage were passed unto the MINLP batch water network model. The results were then used in the original MINLP to get a final solution.

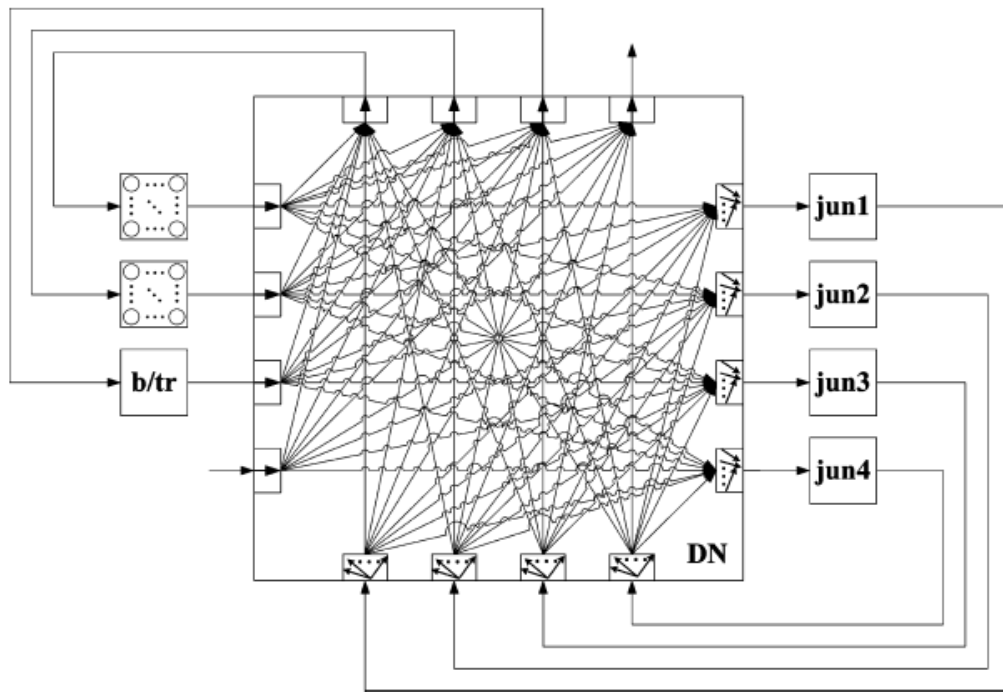


Figure 2.7: Superstructure of Li *et al.* (2010)

Ng *et al.* (2008) extended the concept of regeneration to include the purification of properties other than composition of pollutants. This was called the interception of water streams by interception devices. The aim of such devices was to adjust properties such as pH, conductivity, turbidity, theoretical oxygen demand, color, etc before water streams were reused/recycled. Ng *et al.* (2008) utilized mathematical optimization techniques to identify the optimal allocation and interception of water sources using total annual cost as the objective function. The cost consisted of the price of freshwater, the cost associated with the interception devices and the installation of storage tanks. In addition, the procedure

determined the number and assignment of storage tanks. Similar to Shoaib *et al.* (2008), only indirect reuse between the batch processes was allowed. The storage tanks were also used to store water to and from the interception devices. In the methodology, mass balances were performed around each mixing node and each splitting node. In addition a mixing rule was needed to define all possible mixing patterns among the individual properties. The mixing rule was of the form already given in Equation (2.6). In modeling the interception device, the outlet property operator of a property leaving an interception device was a function of the inlet property operator. The time horizon was discretized into a number of time intervals. The discretization was done in order to link the continuous interception devices with the batch processes. The mathematical model was a MINLP which was solved with a commercial optimization software called extended LINGO which was used to obtain the global solution. The drawback of the method was that it was based on a fixed schedule.

Chen *et al.* (2010) extended the work by Ng *et al.* (2008) to deal with both continuous and batch processes. A continuous process was treated as a special kind of batch process in which the process sources and sinks existed simultaneously over a time interval. Effluent treatment was incorporated to ensure compliance with environmental discharge limits. The objective function of the optimization was to synthesize a property based resource conservation network, PRCN that achieved the minimum freshwater usage for the given problem while satisfying all process and environmental constraints. Similarly, the starting and finishing times of the processes sources and sinks were known beforehand.

2.9 Conclusions

Mathematical formulations are efficient at handling more complex wastewater minimization problems. Many formulations involving wastewater regeneration in batch plants have either been based on single contaminants or on a predefined schedule. It is an oversimplification to assume that the production schedule of the batch plant is known *a priori*. The best model is one that simultaneously determines a cost optimal schedule while fulfilling the batch production requirement and the water requirements in a reasonable computational time.

The above discussion highlights the need for a wastewater minimization methodology that incorporates wastewater regeneration. Moreover, the batch production schedule and water

network that correspond to minimum water requirement ought to be determined simultaneously within the same optimization framework. This dissertation presents a methodology that is aimed at addressing this particular problem. The formulation by Majozi and Gouws (2009) was adopted due to the fact that the formulation was applicable to problems with multiple contaminants and a variable schedule.

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CHAPTER 3

METHODOLOGY DEVELOPMENT

Introduction

This chapter presents the mathematical model for wastewater minimization in batch processes that incorporates regeneration. Majozi and Gouws (2009) developed a mathematical formulation to address wastewater minimization problems with multiple contaminants, whereby the batch production schedule and the minimum wastewater target were obtained simultaneously. Due to this advantage, the formulation is adopted and extended to include wastewater regeneration. The scheduling framework is based on the uneven discretization of the time horizon and the state sequence network, SSN representation of Majozi and Zhu (2001). It is necessary to point out here that the water using batch processes being considered are mass-transfer based operations, i.e., fixed load problems.

3.1 Problem statement

The problem addressed can be stated as follows:

Given:

- (i) the production recipe for each product, including mean processing times in each unit operation,
- (ii) the available units and their capacities,
- (iii) the necessary costs and stoichiometric data,
- (iv) the contaminant mass load of each contaminant,
- (v) water requirement and the cleaning duration for each unit to achieve the required cleanliness,
- (vi) maximum inlet and outlet concentrations of each contaminant,
- (vii) the maximum storage available for water reuse,
- (viii) the performance of the regenerator and
- (ix) the time horizon of interest.

Determine the production schedule that achieves the minimum amount of wastewater generated by utilizing recycle and reuse opportunities in the presence of a central storage vessel and a wastewater regenerator.

3.2 Problem superstructure

The problem superstructure, on which the mathematical formulation is based, is illustrated in Figure 3.1. In the figure, only water-using operations which are part of a complete batch process are depicted. Unit j represents a water-using operation in which the water used consists of freshwater, regenerated water, stored water or recycle/reuse water. Water from unit j can be recycled into the same unit, reused elsewhere or sent to storage. The storage vessel can send water to a unit or to the wastewater regenerator.

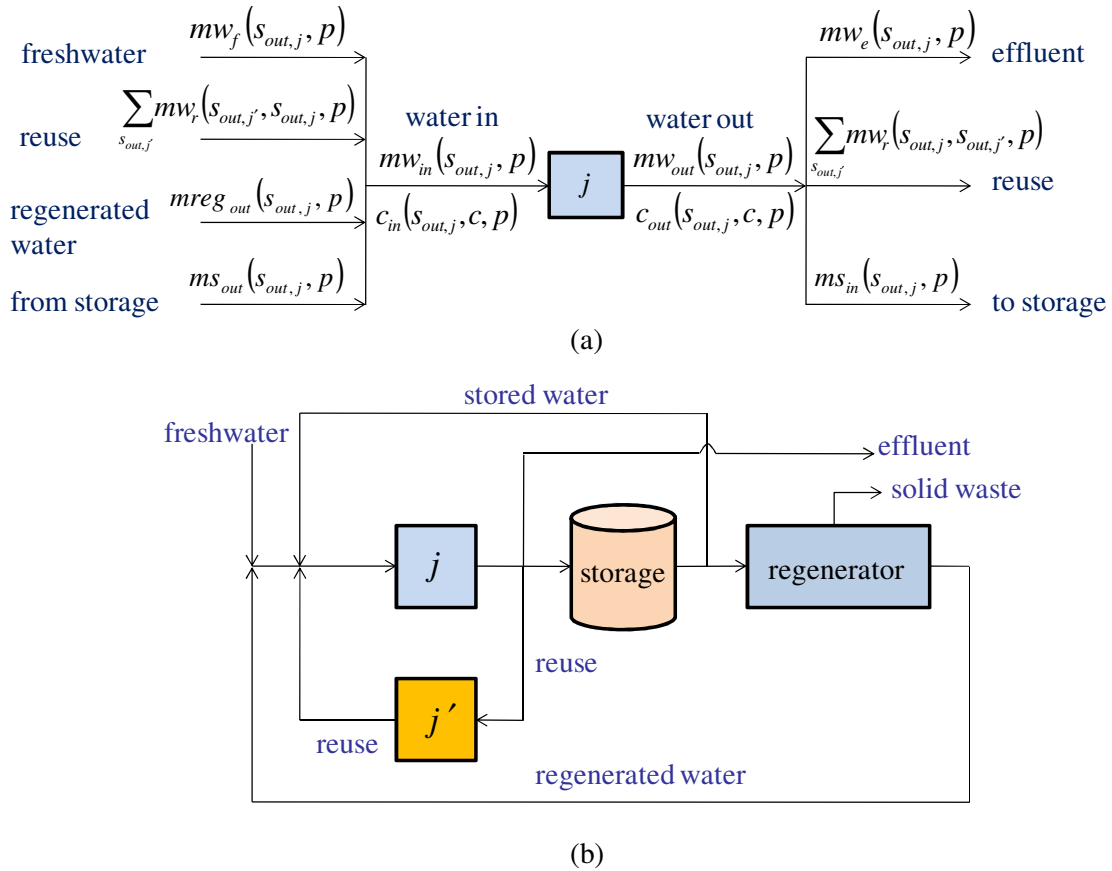


Figure 3.1: Superstructure for the mathematical formulation

The philosophy of operation of the regenerator is as follows:

- (i) water is sent to the regenerator provided there exists an available unit requiring that water. Whenever the regenerator is active, it operates in a continuous mode with steady inlet and outlet streams, until the sink process is satisfied,
- (ii) transfer of water to the regenerator occurs to purify contaminated water because the contaminant concentration of water in storage is too high to be utilized in a unit,
- (iii) transfer of water to the regenerator is through the storage tank, while transfer of regenerated water to a unit is direct,
- (iv) the regenerator operates intermittently in the sense that it is only active if there is a unit that requires water, otherwise it remains in the passive mode and
- (v) the regenerator performance is given in terms of a constant removal ratio of contaminant.

3.3 Mathematical formulation

The constraints in the mathematical formulation are divided into three modules. The first module deals with mass balance constraints, while the second deals with sequencing and scheduling constraints. The constraints in these two modules are associated with wastewater minimization. The third module deals with scheduling of operations for production purposes. All the sets, variables and parameters used in the mathematical formulation can be found in the nomenclature.

3.3.1 Mass balance constraints

It is necessary to define the mass balances around each processing unit, the central storage vessel and the regenerator.

Mass balance around a unit j

Constraint (3.1) is the water balance over the inlet to a unit. Water entering the unit is a combination of freshwater, reuse/recycle streams from other units, j' , water from storage and

water from the regenerator. Constraint (3.2) states that the water leaving a unit could be recycled/reused, discarded as effluent or sent to storage. Constraint (3.3) states that the amount of water exiting a unit must equal the amount of water that entered the unit at the previous time point. This constraint captures the fact that water is not produced in the unit during the washing operation.

$$mw_{in}(s_{out,j}, p) = \sum_{s_{out,j'}} mw_r(s_{out,j'}, s_{out,j}, p) + mw_f(s_{out,j}, p) + ms_{out}(s_{out,j}, p) + mreg_{out}(s_{out,j}, p) \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.1)$$

$$mw_{out}(s_{out,j}, p) = \sum_{s_{out,j'}} mw_r(s_{out,j}, s_{out,j'}, p) + mw_e(s_{out,j}, p) + ms_{in}(s_{out,j}, p) \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.2)$$

$$mw_{in}(s_{out,j}, p-1) = mw_{out}(s_{out,j}, p) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.3)$$

Constraint (3.4) defines the inlet contaminant mass balance. The contaminant mass load in the inlet stream consists of contaminant mass load in recycle/reuse water, the contaminant mass load in water from storage and the contaminant mass load in water from the regenerator. Constraint (3.5) defines the outlet contaminant mass as the mass of contaminant that entered the unit at the previous time point and the mass load of contaminant picked up in the unit during its operation.

$$mw_{in}(s_{out,j}, p)c_{in}(s_{out,j}, c, p) = \sum_{s_{out,j'}} mw_r(s_{out,j'}, s_{out,j}, p)c_{out}(s_{out,j}, c, p) + ms_{out}(s_{out,j}, p)c_{out}(c, p) + mreg_{out}(s_{out,j}, p)cr_{out}(c, p) \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \quad (3.4)$$

$$mw_{out}(s_{out,j}, p)c_{out}(s_{out,j}, c, p) = M(s_{out,j}, c)yw(s_{out,j}, p-1) + mw_{in}(s_{out,j}, p-1)c_{in}(s_{out,j}, c, p-1) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1, c \in C \quad (3.5)$$

Constraints (3.6) and (3.7) ensure that the inlet and outlet contaminant concentrations do not exceed the allowed maximum. Similarly, the maximum allowable water in a unit must not be exceeded. This is governed by Constraint (3.8). Constraints (3.9) to (3.11) restrict the mass of water entering the unit from the various sources to the maximum allowable for the unit. Constraint (3.9) is with respect to recycle/reuse, Constraint (3.10) is with respect to water from storage while Constraint (3.11) is with respect to regenerated water.

$$c_{in}(s_{out,j}, c, p) \leq C_{in}^U(s_{out,j}, c) yw(s_{out,j}, p) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C \quad (3.6)$$

$$c_{out}(s_{out,j}, c, p) \leq C_{out}^U(s_{out,j}, c) yw(s_{out,j}, p - 1) \quad (3.7)$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1, c \in C$$

$$mw_{in}(s_{out,j}, p) \leq Mw^U(s_{out,j}) yw(s_{out,j}, p) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.8)$$

$$mw_r(s_{out,j'}, s_{out,j}, p) \leq Mw^U(s_{out,j}) yw_r(s_{out,j'}, s_{out,j}, p) \quad (3.9)$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P$$

$$ms_{out}(s_{out,j}, p) \leq Mw^U(s_{out,j}) ys_{out}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.10)$$

$$mreg_{out}(s_{out,j}, p) \leq Mw^U(s_{out,j}) yreg_{out}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.11)$$

The maximum quantity of water into a unit is represented by Equation (3.12). It is important to note that for multiple contaminant wastewater, the outlet concentration of the individual components cannot all be set to the maximum, since the contaminants are not limiting simultaneously. The limiting contaminant(s) will always be at the maximum outlet concentration and the non-limiting contaminants will be below their respective maximum outlet concentrations.

$$Mw^U(s_{out,j}) = \max_{c \in C} \left\{ \frac{M(s_{out,j}, c)}{C_{out}^U(s_{out,j}, c) - C_{in}^U(s_{out,j}, c)} \right\}, \forall j \in J, s_{out,j} \in S_{out,j} \quad (3.12)$$

Mass balance around central storage

Constraint (3.13) is the water mass balance around the storage tank. The amount of water stored in the storage tank consists of water stored at the previous time point and the difference between water entering the storage tank from processing unit and water leaving the storage tank either to processing unit or regenerator. Constraint (3.14) defines the initial amount of water in the tank at the start of the time horizon.

$$qw_s(p) = qw_s(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j}, p) - \sum_{s_{out,j}} ms_{out}(s_{out,j}, p) - \sum_{s_{out,j}} mreg_{in}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.13)$$

$$qw_s(p_1) = Qw_s^o - \sum_{s_{out,j}} ms_{out}(s_{out,j}, p_1) - \sum_{s_{out,j}} mreg_{in}(s_{out,j}, p_1) \quad \forall j \in J, s_{out,j} \in S_{out,j} \quad (3.14)$$

The definition of the inlet contaminant concentration to the storage tank is given in Constraint (3.15). The concentration of water exiting the storage tank is assumed to be equal to the concentration of water in the tank as given in Constraint (3.16). This condition is true in the case of perfect mixing. The initial concentration in the storage tank is given in Constraint (3.17). Constraints (3.18) and (3.19) ensure that the maximum capacity of the tank is not exceeded.

$$cs_{in}(c, p) \sum_{s_{out,j}} ms_{in}(s_{out,j}, p) = \sum_{s_{out,j}} (ms_{in}(s_{out,j}, p) c_{out}(s_{out,j}, c, p)) \quad \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (3.15)$$

$$cs_{out}(c, p) \left[\sum_{s_{out,j}} ms_{in}(s_{out,j}, p) + qw_s(p-1) \right] = \left(\sum_{s_{out,j}} ms_{in}(s_{out,j}, p) \right) cs_{in}(c, p) + qw_s(p-1) cs_{out}(c, p-1) \quad \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P, p > p_1 \quad (3.16)$$

$$cs_{out}(c, p_1) = CS_{out}^o(c) \forall c \in C \quad (3.17)$$

$$qw_s(p) \leq Qw_s^U \quad \forall p \in P \quad (3.18)$$

$$ms_{in}(s_{out,j}, p) \leq Qw_s^U y s_{in}(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.19)$$

Constraint (3.20) ensures that no water is stored in the storage vessel at the end of the time horizon. This is in order to give a true optimum, otherwise the minimum target could be misleading.

$$qw_s(p) = 0 \quad \forall p = |P| \quad (3.20)$$

Mass balance around the regenerator

Constraint (3.21) states that the total amount of outlet water from the regenerator at time point p consists of the total amount of inlet water to the regenerator at the previous time point. This constraint captures the assumption that during the operation of the regenerator, no water is produced or lost.

$$\sum_{s_{out,j}} mreg_{in}(s_{out,j}, p-1) = \sum_{s_{out,j}} mreg_{out}(s_{out,j}, p) \quad (3.21)$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1$$

The performance of the regenerator is given in terms of the removal ratio of contaminant, which specifies a constant ratio between the inlet and outlet mass of contaminant. This is stated in Constraint (3.22) for a constant regenerator flowrate.

$$cr_{out}(c, p) = cs_{out}(c, p-1)(1 - RR(c)) \quad \forall c \in C, p \in P, p > p_1 \quad (3.22)$$

The contaminant mass balance around the regenerator is expressed in Constraint (3.23). The contaminant mass load exiting the regenerator to a unit is the difference between the contaminant mass load entering the regenerator and the contaminant mass removed from the water during regeneration, $m_{dirt}(c, p)$.

$$cs_{out}(c, p-1) \sum_{s_{out,j}} mreg_{in}(s_{out,j}, p-1) = cr_{out}(c, p) \sum_{s_{out,j}} mreg_{out}(s_{out,j}, p) + m_{dirt}(c, p) \quad (3.23)$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1$$

3.3.2 Sequencing and scheduling constraints

The scheduling constraints take care of the time dimension associated with batch processes.

The scheduling aspects of the model are divided into four groups as follows:

- those related to task scheduling,
- those that cater for recycle/reuse,
- those that account for the central storage vessel and
- those that account for the regenerator.

Task scheduling

These constraints ensure that each water-using operation is integrated with production scheduling. Constraints (3.24) and (3.25) together ensure that unit j is washed immediately after the task that produced $s_{out,j}$. Constraints assuming the form of Constraints (3.24) or (3.25) are called big-M constraints. If water is used in the unit, $yw(s_{out,j}, p)$ has a value of 1 causing Constraints (3.24) and (3.25) to become active and the start time of washing is forced to coincide with the end time of production. Otherwise, when water is not used in the unit, i.e., $yw(s_{out,j}, p)$ has a value of zero, the two constraints become relaxed. Constraint (3.26) defines the duration of the washing operation performed in unit j . Constraint (3.27) stipulates that the washing operation can only commence at time point p if the task producing $s_{out,j}$ was active at the previous time point.

$$tw_{in}(s_{out,j}, p) \geq t_{out}(s_{out,j}, p) - H(1 - yw(s_{out,j}, p)) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.24)$$

$$tw_{in}(s_{out,j}, p) \leq t_{out}(s_{out,j}, p) + H(1 - yw(s_{out,j}, p)) \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.25)$$

$$tw_{out}(s_{out,j}, p) = tw_{in}(s_{out,j}, p-1) + \tau w(s_{out,j}) yw(s_{out,j}, p-1) \quad (3.26)$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1$$

$$yw(s_{out,j}, p) = y(s_{in,j}^*, p-1) \quad (3.27)$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, s_{in,j}^* \in S_{in,j}^* \rightarrow s_{out,j}, p \in P, p > p_1$$

Recycle/reuse scheduling

Wastewater can only be directly recycled/reused if the unit producing wastewater and the unit receiving wastewater finish operating and begin operating at the same time respectively. Constraint (3.28) describes the relationship between usage of water in a unit and the opportunity for recycle and reuse. The constraint states that for a unit j to transfer water to unit j' , unit j' should require water at that time point. It does not, however, mean that unit j' must use water from unit j , it could still obtain water from other sources. Constraints (3.29) and (3.30) state that the time at which water recycle/reuse takes place coincides with the time at which the water is produced. Constraints (3.31) and (3.32) ensure that the time at which water recycle/reuse takes place coincides with the starting time of the unit receiving the water.

$$yw_r(s_{out,j}, s_{out,j'}, p) \leq yw(s_{out,j'}, p) \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.28)$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \leq tw_{out}(s_{out,j}, p) - H(1 - yw_r(s_{out,j}, s_{out,j'}, p)) \quad (3.29)$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \geq tw_{out}(s_{out,j}, p) - H(1 - yw_r(s_{out,j}, s_{out,j'}, p)) \quad (3.30)$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \leq tw_{in}(s_{out,j}, p) + H(1 - yw_r(s_{out,j}, s_{out,j'}, p)) \quad (3.31)$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \geq tw_{in}(s_{out,j}, p) - H(1 - yw_r(s_{out,j}, s_{out,j'}, p)) \quad (3.32)$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P$$

Central storage scheduling

Constraint (3.33) relates water usage in a unit and water transfer from storage. It states that water can only be transferred to a unit if it uses water at the same time point. However it is not a prerequisite for the unit to use stored water, the water could be provided from other sources. Constraints (3.34) and (3.35) ensure that the time at which water is sent from storage to a unit coincides with the start time of washing of the same unit.

$$ys_{out}(s_{out,j}, p) \leq yw(s_{out,j}, p) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.33)$$

$$ts_{out}(s_{out,j}, p) \geq tw_{in}(s_{out,j}, p) - H(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p)) \\ \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.34)$$

$$ts_{out}(s_{out,j}, p) \leq tw_{in}(s_{out,j}, p) + H(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p)) \\ \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.35)$$

Constraint (3.36) relates water usage in a unit and water transfer to storage. It states that water can only be transferred from a unit to storage if the unit used water at the previous time point. However, washing can take place in the unit without discharging water to the storage tank. The water could be discharged to other sinks. Constraints (3.37) and (3.38) ensure that the time at which water is sent to storage from a unit must coincide with the finishing time of washing of the same unit.

$$ys_{in}(s_{out,j}, p) \leq yw(s_{out,j}, p-1) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.36)$$

$$ts_{in}(s_{out,j}, p) \geq tw_{out}(s_{out,j}, p) - H(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p-1)) \\ \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.37)$$

$$ts_{in}(s_{out,j}, p) \leq tw_{out}(s_{out,j}, p) + H(2 - ys_{out}(s_{out,j}, p) - yw(s_{out,j}, p-1)) \\ \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.38)$$

If water is transferred from storage to a unit at a later time point, the time at which this happens must correspond to a later time in the time horizon. This is specified in Constraint

(3.39). Constraint (3.40) ensures that if water is transferred from a unit to storage at a later time point, the time at which this happens corresponds to a later time in the time horizon.

$$ts_{out}(s_{out,j}, p) \geq ts_{out}(s_{out,j'}, p') - H(2 - ys_{out}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p'))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \quad (3.39)$$

$$ts_{in}(s_{out,j}, p) \geq ts_{in}(s_{out,j'}, p') - H(2 - ys_{in}(s_{out,j}, p) - ys_{in}(s_{out,j'}, p'))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \quad (3.40)$$

Constraints (3.41) and (3.42) state that if water is transferred to storage from more than one unit at the same time point, the time at which they do so must coincide. Constraints (3.43) and (3.44) state that if water is discharged from storage to more than one unit at the same time point, the time at which the water is discharged must coincide.

$$ts_{in}(s_{out,j}, p) \geq ts_{in}(s_{out,j'}, p) - H(2 - ys_{in}(s_{out,j}, p) - ys_{in}(s_{out,j'}, p))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.41)$$

$$ts_{in}(s_{out,j}, p) \leq ts_{in}(s_{out,j'}, p) + H(2 - ys_{in}(s_{out,j}, p) - ys_{in}(s_{out,j'}, p))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.42)$$

$$ts_{out}(s_{out,j}, p) \geq ts_{out}(s_{out,j'}, p) - H(2 - ys_{out}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.43)$$

$$ts_{out}(s_{out,j}, p) \leq ts_{out}(s_{out,j'}, p) + H(2 - ys_{out}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.44)$$

If water is simultaneously being transferred to and discharged from storage, the time at which these happen should coincide. This is given in Constraints (3.45) and (3.46).

$$ts_{in}(s_{out,j}, p) \geq ts_{out}(s_{out,j'}, p) - H(2 - ys_{in}(s_{out,j}, p) - ys_{out}(s_{out,j'}, p))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.45)$$

$$ts_{in}(s_{out,j}, p) \leq ts_{out}(s_{out,j'}, p) - H(2 - ys_{in}(s_{out,j'}, p) - ys_{out}(s_{out,j'}, p))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.46)$$

Constraint (3.47) ensures that if water leaves storage at a later time point compared to water entering storage, the time at which water leaves storage must correspond to a later time in the time horizon.

$$ts_{out}(s_{out,j}, p) \geq ts_{in}(s_{out,j'}, p') - H(2 - ys_{out}(s_{out,j}, p) - ys_{in}(s_{out,j'}, p'))$$

$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \quad (3.47)$$

Regenerator scheduling

Constraint (3.48) defines the relationship between transfer of water to the regenerator and discharge of water from the regenerator. It should be reemphasised at this point that water is only transferred to the regenerator provided that there is a unit available downstream requiring that water and the concentration in the storage unit must exceed the maximum allowed inlet concentration in the receiving unit. Hence, the water transferred to the regenerator at any time is in terms of an available unit. Constraints (3.49) and (3.50) ensure that the time at which water is discharged from the regenerator to a unit coincides with the time at which the unit starts to use water. Constraint (3.51) gives the duration of regeneration.

$$yreg_{out}(s_{out,j}, p) = yreg_{in}(s_{out,j}, p-1) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.48)$$

$$treg_{out}(s_{out,j}, p) \leq tw_{in}(s_{out,j}, p) + H(2 - yreg_{out}(s_{out,j}, p) - yw(s_{out,j}, p))$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.49)$$

$$treg_{out}(s_{out,j}, p) \geq tw_{in}(s_{out,j}, p) - H(2 - yreg_{out}(s_{out,j}, p) - yw(s_{out,j}, p))$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.50)$$

$$treg_{out}(s_{out,j}, p) = treg_{in}(s_{out,j}, p-1) + \left[\frac{\sum_{s_{out,j}} mreg_{in}(s_{out,j}, p-1)}{freg} \right] yreg_{in}(s_{out,j}, p-1)$$

$$\forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.51)$$

Constraint (3.52) ensures that storage does not supply a unit with water through the regenerator and also supply water directly to the unit at the same time point. If the unit is directly supplied with water from storage, the need to regenerate water no longer exists. Constraint (3.53) is included to ensure that the full potential for wastewater regeneration is realised. It states that a unit does not receive water from both the storage tank and the regenerator at the same time point. This is to avoid unnecessary mixing.

$$yreg_{in}(s_{out,j}, p) + ys_{out}(s_{out,j}, p) \leq 1 \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.52)$$

$$yreg_{out}(s_{out,j}, p) + ys_{out}(s_{out,j}, p) \leq 1 \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.53)$$

Constraint (3.54) together with Constraint (3.48) defines the relationship between the usage of water in a unit and the regeneration of water for the unit. Constraint (3.54) states that for water to be charged to the regenerator from storage, the unit requiring the water should begin operation at the next time point. This however, does not mean that the unit cannot begin operation without regenerated water, since water required could be provided from other sources.

$$yw(s_{out,j}, p) \geq yreg_{in}(s_{out,j}, p-1) \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.54)$$

Constraint (3.55) ensures that if water is charged to the regenerator at a later time point, the time at which it does so is at a later time in the time horizon. Constraint (3.56) is similar, but it applies to the time at which water is discharged from the regenerator.

$$treg_{in}(s_{out,j}, p) \geq treg_{in}(s_{out,j'}, p') + H(2 - yreg_{in}(s_{out,j}, p) - yreg_{in}(s_{out,j'}, p')) \\ \forall j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \quad (3.55)$$

$$treg_{out}(s_{out,j}, p) \leq treg_{out}(s_{out,j'}, p') + H(2 - yreg_{out}(s_{out,j}, p) - yreg_{out}(s_{out,j'}, p')) \\ \forall j, j' \in J, s_{out,j} \in S_{out,j}, p, p' \in P, p \geq p' \quad (3.56)$$

3.3.3 Production scheduling constraints

The constraints in this section have been extracted from the work by Majozi and Zhu (2001). They are presented here briefly.

Capacity constraint

The capacity constraint given in Constraint (3.57) ensures that the amount of material processed in unit j at any time point p does not exceed the maximum capacity of the unit.

$$V_j^L y(s_{in,j}^*, p) \leq \sum_{s_{in,j}} m_{in}(s_{in,j}, p) \leq V_j^U y(s_{in,j}^*, p) \quad \forall j \in J, s_{in,j} \in S_{in,j}, s_{in,j}^* \in S_{in,j}^*, p \in P \quad (3.57)$$

Material balance constraints

Constraints (3.58) to (3.64) are the mass balance constraints. These constraints ensure the conservation of mass around each unit.

$$\sum_{s_{in,j}} m_{in}(s_{in,j}, p-1) = \sum_{s_{out,j}} m_{out}(s_{out,j}, p) \quad \forall j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.58)$$

$$q_s(s, p_1) = Q_s^0(s) - m_{in}(s, p_1) \quad s \neq \text{product}, \forall s \in S \quad (3.59)$$

$$q_s(s, p) = q_s(s, p-1) - m_{in}(s, p) \quad s = \text{feed}, \forall s \in S, p \in P, p > p_1 \quad (3.60)$$

$$q_s(s, p) = q_s(s, p-1) + m_{out}(s, p) - m_{in}(s, p) \quad s \neq \text{product}, \text{feed}, \forall s \in S, p \in P, p > p_1 \quad (3.61)$$

$$q_s(s, p_1) = Q_s^0(s) - d(s, p_1) \quad s = \text{product}, \forall s \in S \quad (3.62)$$

$$q_s(s, p) = q_s(s, p-1) + m_{out}(s, p) - d(s, p) \quad s = \text{product}, \text{byproduct}, \forall s \in S, p \in P, p > p_1 \quad (3.63)$$

$$q_s(s, p) \leq Q^U, \forall s \in S, p \in P \quad (3.64)$$

Duration constraints

This constraint addresses the intrinsic aspects of time in batch plants. Constraint (3.65) states that the time at which a particular state is produced is dependent on the duration of the task that produces the same state.

$$t_{out}(s_{out,j}, p) = t_{in}(s_{in,j}^*, p-1) + \tau(s_{in,j}^*)y(s_{in,j}^*, p-1), \\ \forall j \in J, s_{in,j} \in S_{in,j}, s_{in,j}^* \in S_{in,j}^*, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \quad (3.65)$$

3.3.4 Feasibility and time horizon constraints

Constraint (3.66) ensures that if a processing unit j is reusing water from unit j' at time point p , then unit j' cannot reuse water from unit j at the same time point. Constraint (3.67) ensures that at a certain time point both the charging of the regenerator and the discharging from the regenerator on behalf of a particular unit cannot take place at the same time point.

$$yw_r(s_{out,j}, s_{out,j'}, p) + yw_r(s_{out,j'}, s_{out,j}, p) \leq 1 \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.66)$$

$$yreg_{in}(s_{out,j}, p) + yreg_{out}(s_{out,j}, p) \leq 1 \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.67)$$

Constraints (3.68) to (3.74) ensure that each event occurs within the time horizon of time of interest.

$$tw_{in}(s_{out,j}, p) \leq H \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.68)$$

$$tw_{out}(s_{out,j}, p) \leq H \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.69)$$

$$tw_r(s_{out,j}, s_{out,j'}, p) \leq H \quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.70)$$

$$ts_{in}(s_{out,j}, p) \leq H \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.71)$$

$$ts_{out}(s_{out,j}, p) \leq H \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.72)$$

$$treg_{in}(s_{out,j}, p) \leq H \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.73)$$

$$treg_{out}(s_{out,j}, p) \leq H \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \quad (3.74)$$

3.3.5 Objective function

The objective of the formulation depends on whether the production is given or not. In the situation where production is not given, the objective function is expressed as Constraint (3.75). This objective here is the maximization of profit while taking into account freshwater and effluent treatment costs.

$$Max \sum_s \sum_p CP(s)d(s, p) - CF \sum_{s_{out,j}} \sum_p mw_f(s_{out,j}, p) - CE \sum_{s_{out,j}} \sum_p mw_e(s_{out,j}, p) \quad (3.75)$$

Constraint (3.76) is the objective function when the production is given. It is the minimization of effluent.

$$Min \sum_p \left(\sum_{s_{out,j}} mw_e(s_{out,j}, p) \right) \quad (3.76)$$

Due to Constraints (3.4), (3.5), (3.15), (3.16) and (3.23) which involve bilinear terms, the presented mathematical formulation is a MINLP. The method proposed by Majozi and Gouws (2009) was to solve the MINLP using a two step procedure in which the MINLP problem was linearized and solved as a MILP to provide a starting point for the exact MINLP problem. The method of linearization is discussed in the Appendix.

3.4 Practical application

Firstly, it is important to identify the section of the plant to which this methodology will be applied. Once this is identified, information pertinent to the operation of the plant as stipulated in Section 3.1 is required. These values can be obtained based on thermodynamic data (inlet and outlet concentrations) or based on experience from working on the plant. The contaminants present on the plant should be identified and a careful consideration should be made about the most suitable regenerator to employ. The removal ratio for contaminants in the regenerator can be obtained from information about the purity level achievable by the chosen regenerator.

In the situation whereby the freshwater available contains some impurities, a new variable representing the contaminant concentration of the freshwater, $c_f(c, p)$, is introduced to the formulation. Constraint (3.4) must be modified to account for the contaminant mass load entering with impure freshwater to unit j . This is given in Constraint (3.4b). The rest of the mathematical formulation remains unchanged in the presence of impure freshwater.

$$\begin{aligned}
 mw_{in}(s_{out,j}, p)c_{in}(s_{out,j}, c, p) = & mw_f(s_{out,j}, p)c_f(c, p) + \\
 & \sum_{s_{out,j'}} mw_r(s_{out,j'}, s_{out,j}, p)c_{out}(s_{out,j}, c, p) + \\
 & ms_{out}(s_{out,j}, p)cs_{out}(c, p) + \\
 & mreg_{out}(s_{out,j}, p)cr_{out}(c, p) \\
 & \forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C
 \end{aligned} \tag{3.4b}$$

Next, the minimum wastewater target and the corresponding batch production schedule are determined from the application of the methodology. Once these have been obtained, the plant can be operated in like manner.

In the succeeding chapter, the methodology is applied to a few case studies to buttress this point.

References

Majozi, T., & Zhu, X.X. (2001). A novel continuous time MILP formulation for multipurpose batch plants. 1. Short-term scheduling. *Ind. Eng. Chem. Res.*, 40 (25), 5935-5949

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CHAPTER 4

CASE STUDIES

In this chapter the application of the regeneration methodology is demonstrated through two problems, one from literature and the other from a practical production facility.

4.1 Literature example

The example considered is a well-published multipurpose facility which is commonly known as BATCH 1 in literature. The facility consists of three different chemical reactions which can be performed in two common reactors. In addition, a heater exists for heating Feed A before reaction and a separator exists to purify product from Reaction 3. The STN and SSN representation for the literature example are given in Figure 4.1.

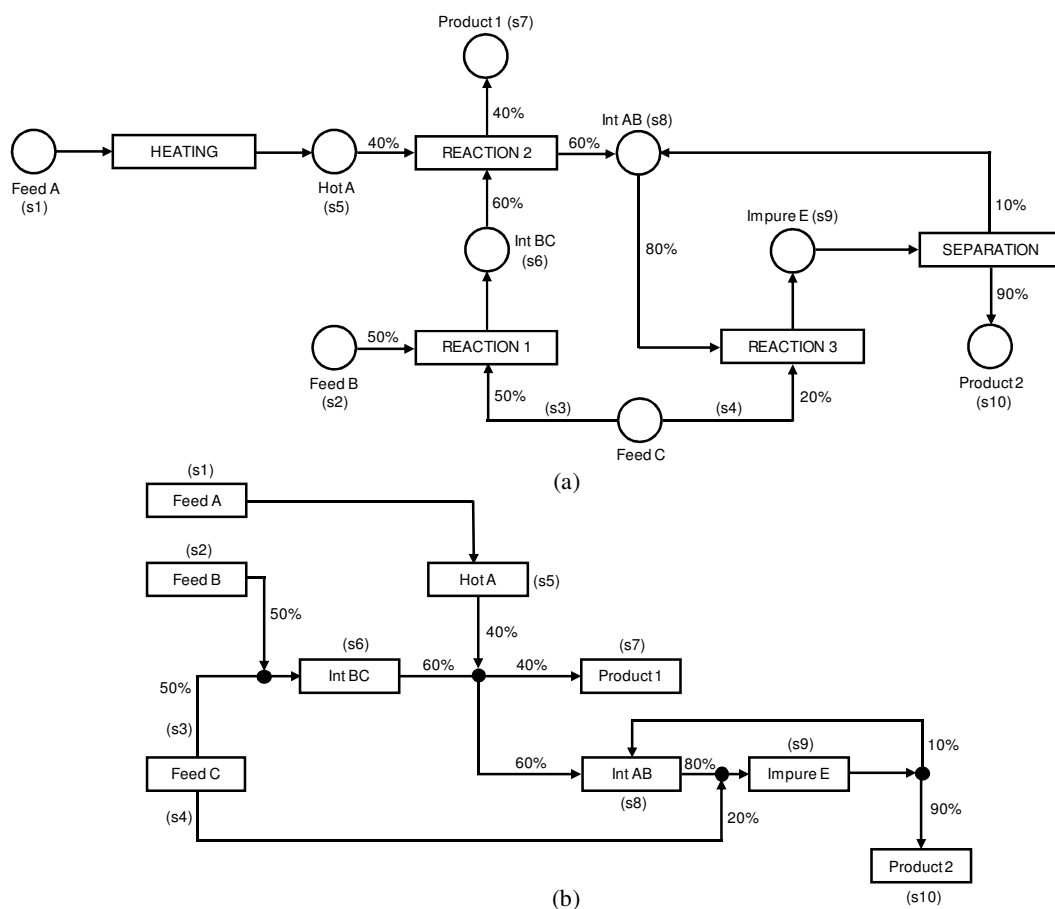


Figure 4.1: (a) STN and (b) SSN for the literature example

The data required for production scheduling are given Table 4.1.

Table 4.1: Data required for production scheduling in literature example

Units	Capacity	Suitability	Mean processing time (τ)
Heater	100	Heating	1
Reactor 1	50	Reaction 1,2,3	2,2,1
Reactor 2	80	Reaction 1,2,3	2,2,1
Still	200	Separation	1 for product 2, 2 for IntAB
States	Storage capacity	Initial amount	Price
Feed A	Unlimited	Unlimited	0
Feed B	Unlimited	Unlimited	0
Feed C	Unlimited	Unlimited	0
Hot A	100	0	0
IntAB	200	0	0
IntBC	150	0	0
Impure E	200	0	0
Product 1	Unlimited	0	100
Product 2	Unlimited	0	100

Similar to the work by Majozi and Gouws (2009), the philosophy is that after a reaction has taken place in a reactor, the reactor must be washed before another reaction can take place. This ensures that any product residue is removed to ensure the integrity of subsequent product. Data pertaining to the washing operations is given in Table 4.2. In addition, the cost of freshwater is given as 2 c.u./kg water whilst the effluent treatment cost is 3 c.u./kg.

A central storage tank for wastewater is available with a capacity of 200 kg. At the beginning of the time horizon, the central storage tank is empty. The flowrate of the regenerator is given to be 100 kg/h. The removal ratios of the various contaminants are provided in Table 3. The objective function is the maximization of profit as given in Constraint (3.75). The time horizon of interest is 10 h.

Table 4.2: Wastewater minimization data for literature example

		Maximum concentration (g contaminant/kg water)		
		Contaminant 1	Contaminant 2	Contaminant 3
Reaction 1 (Reactor 1)	Max. inlet	0.5	0.5	2.3
	Max. outlet	1	0.9	3
Reaction 2 (Reactor 1)	Max. inlet	0.01	0.05	0.3
	Max. outlet	0.2	0.1	1.2
Reaction 3 (Reactor 1)	Max. inlet	0.15	0.2	0.35
	Max. outlet	0.3	1	1.2
Reaction 1 (Reactor 2)	Max. inlet	0.05	0.2	0.05
	Max. outlet	0.1	1	12
Reaction 2 (Reactor 2)	Max. inlet	0.03	0.1	0.2
	Max. outlet	0.075	0.2	1
Reaction 3 (Reactor 2)	Max. inlet	0.3	0.6	1.5
	Max. outlet	2	1.5	2.5
		Mass load (g)		
		Contaminant 1	Contaminant 2	Contaminant 3
Reaction 1	Reactor 1	4	80	10
	Reactor 2	15	24	358
Reaction 2	Reactor 1	28.5	7.5	135
	Reactor 2	9	2	16
Reaction 3	Reactor 1	15	80	85
	Reactor 2	22.5	45	36.5
		Duration of washing (h)		
		Reaction1	Reaction2	Reaction3
Reactor 1		0.25	0.5	0.25
Reactor 2		0.3	0.25	0.25

Table 4.3: Removal ratio for contaminants

Contaminant	Removal ratio
Contaminant 1	0.98
Contaminant 2	0.97
Contaminant 3	0.96

4.1.1 Results and discussion

The resulting model for the literature example was formulated in GAMS 22.0 and solved using the DICOPT2 algorithm, with CPLEX 9.1.2 as the MIP solver and CONOPT3 as the NLP solver. The model had 532 binary variables. The optimum number of time points was 10. The value of the objective function, the maximization of profit in Constraint (3.75), was 21129 c.u.

The optimum amount of freshwater used was 401.7 kg. If regeneration was not considered the objective function was 20180 c.u. with an optimum freshwater usage of 479 kg. The incorporation of the regenerator resulted in a 4.7% increase in profit and a 19.24% decrease in effluent production. The solution time was 46.3 seconds using a Pentium 4, 3.4 GHz processor. The schedule corresponding to the MILP was infeasible. Hence, the resulting solution of 21129 c. u. is a local optimum. The schedule obtained from the optimization is shown in Figure. 4.2.

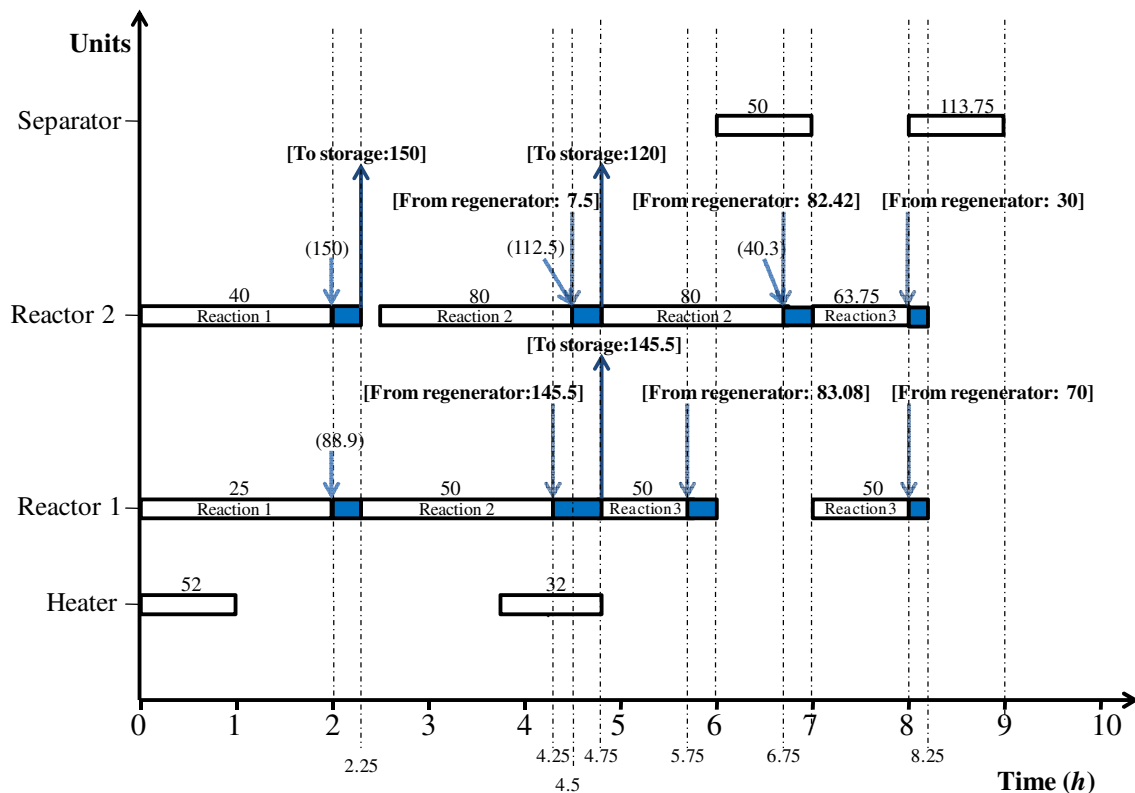


Figure 4.2: Resulting production schedule for literature example

In Figure 4.2, the clear blocks represent the production operation in the unit while the dark blocks represent the washing operation in the unit. The numbers above the clear blocks represent the amount of material used in the unit for production. The numbers in brackets represent freshwater, the sum of these amount to 401.7 kg, hence the target. Water transfer to and from storage as well as water transfer from regenerator have been clearly labelled.

From Figure 4.2, it can be seen that reaction 1 occurs twice and reactions 2 and 3 occur thrice. The water used for washing Reactors 1 and 2 (R1 and R2) consists of freshwater only. 150 kg of water produced in R2 after washing is sent to storage at 2.25h. This provides opportunity for indirect water reuse or wastewater regeneration. The storage tank discharges 145.5 kg of water to the regenerator with respect to R1 at 2.80h. Regenerated water is discharged to R1 at 4.25h for washing. The storage tank later discharges 7.5 kg of water to the regenerator with respect to R2 at 4.43h. Regenerated water is discharged to R2 at 4.5h for washing. A similar scenario is encountered with water sent to storage from R2 and R1 at 4.75h. Regenerated water is utilized in the later washing operations that follow. It can be observed from this solution that direct water reuse between units did not occur.

4.2 Industrial case study

This case study is based on a section of a pharmaceuticals production plant which produces 4 types of products, viz., shampoos, deodorants, lotions and creams. 4 mixers for product mixing were available in this section. Each product was produced by a specific mixer. Mixer 1 was dedicated to the mixing of shampoos, mixer 2 was dedicated to the mixing of deodorants, mixer 3 was dedicated to the mixing of lotions and mixer 4 was dedicated to the mixing of creams. The general production procedure is as follows. Raw material is charged to a mixer. The raw material is then mixed until the required physical characteristics are obtained. Once a product is mixed, it is removed and stored. The mixers are then washed. There is sufficient storage available for product. The typical production requirement over a 24 hour time horizon is given in Table 4.4. In Table 4.4, the average production time for each product is also given.

The data pertaining to wastewater minimization is given in Table 4.5 together with the residue mass left in each mixer after product has been removed. These are average values

taken from actual process data. The maximum outlet concentrations from each mixer are also given. It is important to note that there is maximum outlet concentration defined for only one component from each mixer. This is since each mixer will at any point only contain residue of a specific product. Also given is the maximum contaminant load that can enter with the water for a cleaning operation. In this problem, the residue left from the specific product in a mixer accounts for the contaminant mass added to water. This then makes the limiting component in each mixer the component that leaves residue in the mixer. For example mixer 1 has shampoo as the limiting contaminant, since this is the only component which leaves a residue in the mixer. The limiting amount of water for each mixer is calculated using Equation (3.12) and is given for each mixer in Table 4.5.

A central storage vessel with a capacity of 10 tons is available for storing wastewater used for washing. At the beginning of the time horizon, the central storage vessel is empty. The washing of each mixer takes 30 minutes.

Table 4.4: Production data for industrial case study

Mixer	Product	Number of batches	Duration (h)
1	Shampoo	2	7
2	Deodorant	3	5.5
3	Lotion	1	11
4	Cream	2	11

Table 4.5: Wastewater minimization data for industrial case study

Mixer	Contaminant	Residue mass (kg)	Limiting water (kg)	$C^{\max}$ outlet (kg/kg)
1	Shampoos	15	576.9	0.04
2	Deodorants	15	361.4	0.045
3	Lotions	30	697.6	0.05
4	Creams	70	1238.9	0.06

The maximum inlet concentration of each mixer is given in Table 4.6. In this case, the maximum inlet concentration of deodorant in mixers 1, 3 and 4 is set to zero. This is because the reuse of wastewater containing deodorant in a mixer with any other residue is

undesirable. However, wastewater containing deodorant can be reused in a cleaning operation in mixer 2, containing another deodorant residue.

Table 4.6: Maximum inlet concentrations for cleaning operation in the industrial case study

Mixer	Shampoo (kg product/ kg water)	Deodorant (kg product/ kg water)	Lotion (kg product/ kg water)	Creams (kg product/ kg water)
1	0.014	0	0.007	0.0035
2	0.014	0.0035	0.007	0.007
3	0.014	0	0.007	0.0035
4	0.014	0	0.007	0.0035

A regenerator with a flowrate of 466 kg/h is available. The removal ratio of the various contaminants is given in Table 4.7.

Table 4.7: Removal ratio for contaminants

Contaminant	Removal ratio
Shampoo	0.95
Deodorant	0.99
Lotion	0.96
Cream	0.98

4.2.1 Results and discussion

The industrial case study was formulated using the presented methodology in GAMS 22.0 and solved using the DICOPT2 algorithm, with CPLEX 9.1.2 as the MIP and CONOPT3 as the NLP solvers. The resulting model had 576 binary variables. The optimum number of time points was 16. The value of the objective function, which was the minimization of effluent as given in Constraint (3.76), was 2653 kg of water. If regeneration was not considered the objective function was 3587 kg of water. The incorporation of the regenerator resulted in a 26% decrease in effluent production. The solution time was 464 seconds using a Pentium 4, 3.4 GHz processor. The schedule corresponding to the MILP was infeasible. Hence, the resulting solution of 2653 kg is a local optimum.

The resulting schedule of the solution is given in Figure 4.3. The clear blocks represent the production operation in the unit while the dark blocks represent the washing operation in the unit. The numbers in round brackets represent freshwater. The sum of these amount to 2653 kg, hence the target. The numbers in square brackets represent direct reuse water. Water transfer to and from storage as well as water transfer from regenerator have been clearly labelled.

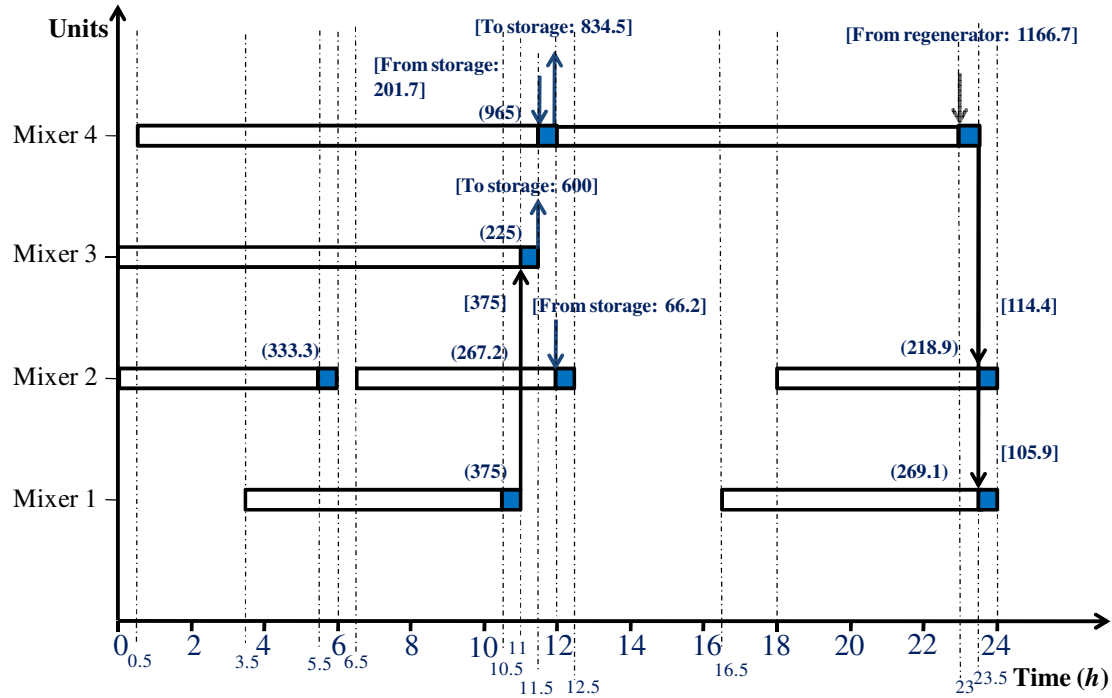


Figure 4.3: Production schedule for the industrial case study

From the Gantt chart in Figure 4.3, it can be observed that the schedule meets the production requirement, i.e. 2 batches of shampoo, 3 batches of deodorant, one batch of lotion and 2 batches of cream. Mixer 3 uses freshwater in addition to direct reuse water from mixer 1. Mixer 3 sends 600 kg of water to storage at 11.5h. Of this water, 201.7 kg is indirectly reused in mixer 4 at 11.5h. At 20.2h the storage tank discharges 1166.7 kg of water to the regenerator on behalf of mixer 4. At 23h, the regenerated water is discharged to mixer 4. The rest of the production schedule can be observed from the Figure 4.3. As mentioned earlier, it is not acceptable to use water from mixer 2 containing deodorant. This was ensured in the model by setting the binary variable associated with water transfer from mixer 2 to any other mixer to zero and also by setting the binary variable associated with mixer 2 transferring



water to the storage tank to zero. These conditions were met, as can be seen from the Gantt chart.

References

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CHAPTER 5

CONCLUSIONS

5.1 Conclusions

Presented in this dissertation is a methodology for wastewater minimization in batch plants that incorporates a regenerator. The methodology is applicable to multipurpose plants containing multiple contaminants. The particular advantage of this work is that it does not require the batch production schedule to be given beforehand. The resulting formulation is a MINLP for which global optimality cannot be guaranteed.

The effectiveness of the methodology was demonstrated by applying it to an illustrative example and an industrial case study. In the illustrative example, a 19.2% reduction in wastewater generation was achieved when compared to the situation that exploited only direct reuse between water-using operations and indirect reuse with storage. Similarly, in the industrial case study, a 26% reduction in wastewater was achieved. In both cases, the batch production schedule corresponding to the minimum wastewater was determined.

5.2 Recommendation

The model has a considerable number of bilinear terms. Upon linearization, additional variables and constraints are introduced in the model which results in the model being very large. It is recommended that different scheduling methods be considered in the wastewater minimization methodology to investigate the effect on computational times and wastewater minimization results.

APPENDIX

The presented mathematical formulation is a MINLP for which global optimality cannot be guaranteed. The mathematical formulation is nonlinear due to the bilinear terms in Constraints (3.4), (3.5), (3.15), (3.16) and (3.23). However, a method employed by Majozi and Gouws (2009) was used to determine whether a given solution was global or local. The method involved a two step procedure in which the MINLP problem was linearized and solved as a MILP to provide a starting point for the exact MINLP problem. The method of linearization is discussed below. Consider Constraint (3.4) containing the following bilinear terms:

- i. $mw_{in}(s_{out,j}, p)c_{in}(s_{out,j}, c, p)$
- ii. $mw_r(s_{out,j'}, s_{out,j}, p)c_{out}(s_{out,j}, c, p)$
- iii. $ms_{out}(s_{out,j}, p)cs_{out}(c, p)$
- iv. $mreg_{out}(s_{out,j}, p)cr_{out}(c, p)$

These terms are linearized using the method by Sherali & Alameddine (1992) as discussed by Quesada and Grossmann (1995) given below:

Let :

$$mw_{in}(s_{out,j}, p)c_{in}(s_{out,j}, c, p) = \Gamma_1(s_{out,j}, c, p)$$

$$mw_r(s_{out,j'}, s_{out,j}, p)c_{out}(s_{out,j}, c, p) = \Gamma_2(s_{out,j'}, s_{out,j}, c, p)$$

$$ms_{out}(s_{out,j}, p)cs_{out}(c, p) = \Gamma_3(s_{out,j}, c, p)$$

$$mreg_{out}(s_{out,j}, p)cr_{out}(c, p) = \Gamma_4(s_{out,j}, c, p)$$

With each variable having the following bounds:

$$0 \leq mw_{in}(s_{out,j}, p) \leq Mw^U(s_{out,j})$$

$$\begin{aligned}0 &\leq c_{in}(s_{out,j}, c, p) \leq C_{in}^U(s_{out,j}, c) \\0 &\leq mw_r(s_{out,j'}, s_{out,j}, p) \leq Mw^U(s_{out,j}) \\0 &\leq c_{out}(s_{out,j}, c, p) \leq C_{out}^U(s_{out,j}, c) \\0 &\leq ms_{out}(s_{out,j}, p) \leq Mw^U(s_{out,j}) \\0 &\leq cs_{out}(c, p) \leq CS_{out}^U(c) \\0 &\leq mreg_{out}(s_{out,j}, p) \leq Mw^U(s_{out,j}) \\0 &\leq cr_{out}(c, p) \leq CR_{out}^U(c)\end{aligned}$$

The following are true for Γ_1 :

$$\Gamma_1(s_{out,j}, c, p) \geq 0, \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.1)$$

$$\begin{aligned}\Gamma_1(s_{out,j}, c, p) &\geq Mw^U(s_{out,j})c_{in}(s_{out,j}, c, p) + mw_{in}(s_{out,j}, p)C_{in}^U(s_{out,j}, c) - \\&\quad Mw^U(s_{out,j})C_{in}^U(s_{out,j}, c), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P\end{aligned} \quad (A.2)$$

$$\Gamma_1 \leq Mw^U(s_{out,j})c_{in}(s_{out,j}, c, p), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.3)$$

$$\Gamma_1 \leq mw_{in}(s_{out,j}, p)C_{in}^U(s_{out,j}, c), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.4)$$

The following are true for Γ_2 :

$$\Gamma_2(s_{out,j'}, s_{out,j}, c, p) \geq 0, \forall j, j' \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.5)$$

$$\begin{aligned}\Gamma_2(s_{out,j'}, s_{out,j}, c, p) &\geq Mw^U(s_{out,j})c_{out}(s_{out,j'}, c, p) + mw_r(s_{out,j'}, s_{out,j}, p)C_{out}^U(s_{out,j'}, c) \\&\quad - Mw^U(s_{out,j})C_{out}^U(s_{out,j'}, c), \forall j, j' \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P\end{aligned} \quad (A.6)$$

$$\begin{aligned}\Gamma_2(s_{out,j'}, s_{out,j}, c, p) &\leq Mw^U(s_{out,j})c_{out}(s_{out,j'}, c, p) \\&\quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P\end{aligned} \quad (A.7)$$

$$\begin{aligned}\Gamma_2(s_{out,j'}, s_{out,j}, c, p) &\leq mw_r(s_{out,j'}, s_{out,j}, p)C_{out}^U(s_{out,j'}, c), \\&\quad \forall j, j' \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P\end{aligned} \quad (A.8)$$

The following are true for Γ_3

$$\Gamma_3(s_{out,j}, c, p) \geq 0, \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.9)$$

$$\Gamma_3(s_{out,j}, c, p) \geq Mw^U(s_{out,j})cs_{out}(c, p) + ms_{out}(s_{out,j}, p)CS_{out}^U(c) - Mw^U(s_{out,j})CS_{out}^U(c), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.10)$$

$$\Gamma_3(s_{out,j}, c, p) \leq Mw^U(s_{out,j})cs_{out}(c, p), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.11)$$

$$\Gamma_3(s_{out,j}, c, p) \leq ms_{out}(s_{out,j}, p)CS_{out}^U(c), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.12)$$

The following are true for Γ_4

$$\Gamma_4(s_{out,j}, c, p) \geq 0, \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.13)$$

$$\Gamma_4(s_{out,j}, c, p) \geq Mw^U(s_{out,j})cr_{out}(c, p) + mreg_{out}(s_{out,j}, p)CR_{out}^U(c) - Mw^U(s_{out,j})CR_{out}^U(c), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.14)$$

$$\Gamma_4(s_{out,j}, c, p) \leq Mw^U(s_{out,j})cr_{out}(c, p), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.15)$$

$$\Gamma_4(s_{out,j}, c, p) \leq mreg_{out}(s_{out,j}, p)CR_{out}^U(c), \forall j \in J, s_{out,j} \in S_{out,j}, c \in C, p \in P \quad (A.16)$$

Substituting the above linearized variables into Constraint (3.4) gives Constraint (A.17):

$$\Gamma_1(s_{out,j}, c, p) = \sum_{s_{out,j'}} \Gamma_2(s_{out,j'}, s_{out,j}, c, p) + \Gamma_3(s_{out,j}, c, p) + \Gamma_4(s_{out,j}, c, p) \quad (A.17)$$
$$\forall j, j' \in J, s_{out,j} \in S_{out,j}, p \in P, c \in C$$

The bilinear terms in Constraints (3.5), (3.15), (3.16) and (3.23) are linearized in a similar manner and substituted in the original constraints to yield new constraints similar to Constraint (A.17).

Solution procedure

The relaxed MILP problem consists of Constraints (3.1) to (3.74), (3.75) or (3.76) with the new substituted constraints instead of Constraints (3.4), (3.5), (3.15), (3.16) and (3.23). Also included are the respective forms of Constraints (A.1) to (A.4) for each linearized variable. The relaxed MILP problem is solved to provide a starting point for the exact MINLP problem. The solution procedure is illustrated in Figure A.1.

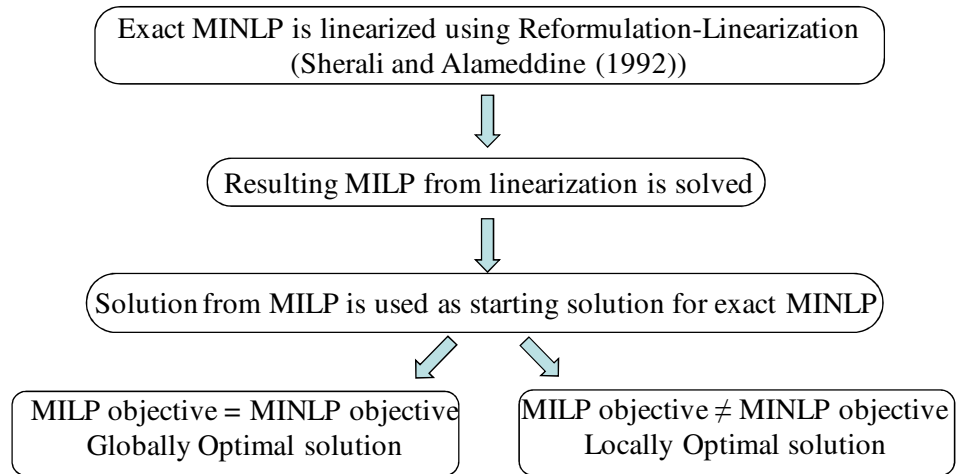


Figure A.1: Solution procedure