DEVELOPMENT OF A COMPLETE PROCESS INTEGRATION FRAMEWORK FOR WASTEWATER MINIMISATION IN MULTIPURPOSE BATCH PLANTS

Report to the

Water Research Commission

by

T Majozi and JF Gouws

Department of Chemical Engineering,

University of Pretoria

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EXECUTIVE SUMMARY

1. INTRODUCTION

Wastewater minimisation in the processing industry is becoming ever more important as sources of fresh water become limited and environmental legislation becomes more stringent. Wastewater minimisation is especially important in a country like South Africa which has awakened to the fact that water is no longer an abundant, but a scarce resource. This has prompted researchers in the industry to look into cost effective means of reducing effluent discharged into the environment. In the past, however, much focus has been on continuous processes and the reduction of wastewater within these processes, rather than batch processes.

The inherent time difficulties with batch processes have prompted much research into the scheduling of the processes. In the last few years scheduling methodologies have been developed that have structures that lend themselves to be extended to include wastewater minimisation.

The main objective of this project is to develop a mathematical optimisation technique for wastewater minimisation that could be applied to industrial scale problems. It has been noted from literature that there does not exist a wastewater minimisation methodology that effectively takes multiple contaminant wastewater into consideration. However, multiple contaminant wastewater systems are more representative of practical situations.

2. ADOPTED APPROACH

The adopted approach was to first undertake a detailed literature survey. This provided insight into gaps in current research and limitations of previous methodologies. The second step was the derivation of a mathematical methodology that addressed the shortcomings of previous methodologies. Following this, an industrial site was identified for the application of the derived mathematical methodology. The final step in the approach was to apply the methodology to the industrial case site.

3. LITERATURE REVIEW

Scheduling in Batch Processes

The general scheduling problem entails the determination of the optimal sequence of events using the available resources. The systematic formulation for this problem was initially given by Sparrow et al. (1975) as an MINLP problem.

Scheduling techniques can be divided into two groups based on the time horizon representation, namely discrete time and continuous time formulations. Due to its fewer binary variables, the continuous time formulation has received much interest over the past years. Ierapetritou and Floudas (1998) developed a formulation using a state task network. Two important ideas were introduced in the formulation. Firstly, the time horizon was not represented by time slots but rather distinct points called event points. The next important idea is the decoupling of task events from unit events. Based on the event point representation, Majozi and Zhu (2001) derived a scheduling formulation. Due to the binary variable assignment to an effective state, the number of binary variables resulting from the formulation was much less than in other formulations. Thus the solution to the problem was not so computationally intensive. This formulation also resulted in a mixed integer linear program.

Wastewater Minimisation in Batch Processes

Wastewater minimisation in batch processes has gained some interest in the research community in the past ten years. This is mainly due to environmental pressure and derivation of more effective scheduling methodologies. Wastewater minimisation in batch plants can be roughly divided into two categories, namely graphical techniques (Wang & Smith, 1995; Majozi et al., 2006; Foo et al., 2005) and mathematical techniques (Almató et al., 1997; Grau et al., 1996; Majozi, 2005).

Graphical techniques have the advantage of giving insight into the operations that are restricting the reuse of wastewater. However, graphical techniques are generally based on the schedule being determined beforehand, which means the wastewater target is not necessary the absolute minimum. Mathematical techniques have the advantage of being able to deal with multiple contaminant systems and determine the wastewater target at the same time as the schedule. However, mathematical techniques tend to be a black box type of approach and give little insight into the operations restricting reuse.

4. MATHEMATICAL MODELS DEVELOPED

From the literature survey it was concluded that multiple contaminant wastewater minimisation has not been dealt with effectively in the past. Based on this, two methodologies were derived. The first methodology minimises wastewater where there were multiple contaminants present and only a single storage vessel available. The second methodology minimises wastewater where there are multiple contaminants present and multiple storage vessels.

Multiple Contaminant Wastewater Minimisation (Majozi & Gouws, 2007)

The methodology deals with wastewater minimisation in a multiple contaminant environment. The methodology is based on a superstructure approach which makes it applicable to a wider range of operations. Mass balance constraints and scheduling constraints are taken into account. Wastewater is minimised through maximising the recycle and reuse of wastewater. The methodology determines the schedule that will generate the least amount of wastewater.

Multiple Contaminant Wastewater Minimisation with Multiple Storage Vessels

The multiple contaminant wastewater minimisation methodology derived was extended to include multiple storage vessels. The methodology is able to take specific storage needs into consideration. This finds application in situations where wastewater containing different contaminants is not allowed to be mixed. To maximise the reuse opportunities in a situation, each wastewater stream can be stored in a separate storage vessel. The methodology once again determines the schedule that will produce the least amount of wastewater.

5. PRACTICAL IMPLEMENTATION OF METHODOLOGY

Industrial Site Background

The operation at the industrial site produces mainly liquid products and women’s sanitary products. The plant operates mainly in batch mode when producing the liquid products. This is due to the need to produce a wide variety of products in small amounts. Water usage on site averages about 90 000 m^3 per annum.

The plant can roughly be divided into three main sections, namely the pharmaceutical mixing area, the toiletries mixing area and the women's sanitary product area. As the water usage was highest in the pharmaceutical and toiletries area, these areas became the main focus of water minimisation. The water usage at the industrial site is shown in Figure 1.

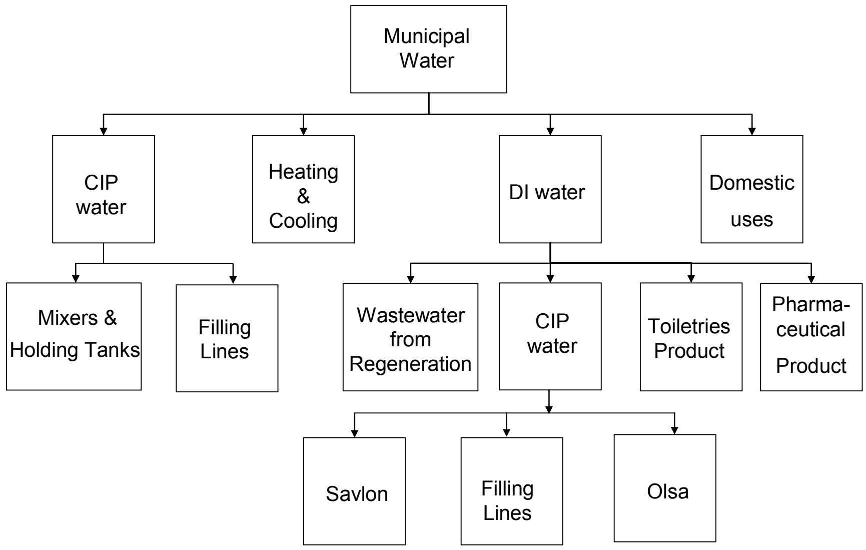

Figure 1. Breakdown of municipal water usage at the industrial site

Application of Mathematical Methodology at the Industrial Site

Currently the operation at the industrial site has no formal scheduling methodology or water saving strategy. Upon assessment of the plant, the area where scheduling together with wastewater minimisation could take place was the toiletries mixing area.

The application of the mathematical methodology was done in three steps. The first step was a preliminary application of the methodology to the mixing area to identify data that was needed and practical considerations that needed to be taken into account. The second step took some practical considerations into account, more specifically the compatibility of washout water and product residue. The final step was the development of a model that could be applied in practice.

First investigation

As a preliminary study into the operation at the industrial site, the process was modelled in a simplified manner, as a single contaminant system. The single contaminant methodology derived by Majozi (2005) was applied to the toiletries mixing area. This gave insight into any practical considerations and possible inaccuracies with data used.

The resulting model was solved for various scenarios and the following was concluded from the investigation:

- Compatibility of wastewater and product residue needed to be taken into account
- Corporate requirements for reuse of water needed to be checked
- Preferential mixing of certain products in certain mixers needed to be addressed
- Consideration of different washout steps might need addressing
- Different sized mixers need to be taken into account
- More accurate outlet concentrations are needed, and
- Water amounts for washouts should be investigated.

Furthermore, the model drastically increased in size, with long solution times, when the product storage vessels were taken into consideration.

From the above results a second, more detailed model was derived for the mixing area.

Secondary study

Compatibility between wastewater and product residue has to be taken into account when one is considering reuse of washout water containing product. Product residue and contaminant compatibilities can only effectively be dealt with by seeing the problem as a multiple contaminant problem. The methodology by Majozi (2005) was extended by Majozi and Gouws (2007) to include multiple contaminants and was applied to the operation at the industrial site.

This model was solved for different production requirements. The model derived under these circumstances was not necessarily practically implementable. This was due to the need for changes in the method of washout, i.e. changing from a continuous type washout to a batch type washout, and concerns over the general lack of data on the reuse of washout water. However, due to the change from chemical sanitising to heat sanitising the opportunity arose to derive a model based on this with practical applicability.

Final Model

A final model was derived for application at the industrial site. The water considered for reuse in this model was the water used for the sanitising step of the washout. This water lends itself to reuse as the water contains low levels of contaminants and is sanitary due to the elevated temperature of the water. There is an intermediate storage tank available for the water, the cleaning in place (CIP) tank. Therefore, there was no need to purchase any equipment to implement the methodology.

An example of the schedule found by the final model is given below. For the example the four toiletries mixers were scheduled with the minimisation of wastewater as the main objective. Four different products were mixed and the time horizon was 24 hours. Within this time horizon two batches of a shampoo, three batches of a lotion, two batches of a deodorant and two batches of a cream needed to be produced. The mixing times are given in Table 1.

Table 1. Mixing times

	Mixer 1 (hr)	**Mixer 2 (hr)**	**Mixer 3 (hr)**	**Mixer 5 (hr)**
Shampoo	8	8	8	8
Lotion	5	4	5	4
Deo	7	6	7	5
Cream	12	11	12	10

In this example it was assumed that the amount of water used for the sanitising step was 500 l. The resulting schedule is given in Figure 2. The total amount of effluent from all the sanitising steps at the end of the time horizon was 500 l. The dashed arrows in the figure show reused water entering a vessel from the CIP tank for a washout and the solid arrows show sanitising water going to the CIP tank for reuse later. The washout of mixer one, after the first batch of shampoo, uses fresh water and no sanitising water, since it is the first washout in the time horizon. At the end of the time horizon the sanitising water from the washout of mixer two, after the batch of cream, goes to effluent. This is because this is the last washout in the time horizon.

Using the above model the amount of water used in each washout is decreased by the amount of water used for the sanitising step. This amount is between 22% and 55% per washout, depending on the length on the sanitising step.

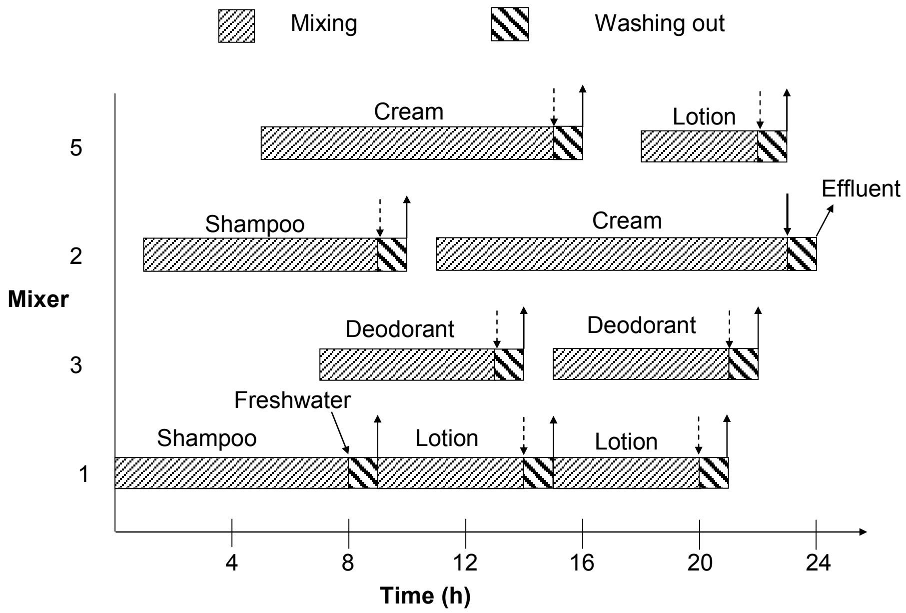

Figure 2. Example of the production schedule generated from the final model

Water Savings From Process Changes

Observations on the plant indicated that there were many opportunities for saving water through process related changes, specifically with the water used for the sanitising step in a washout and the water used for temperature control. As part of the broader objective of water savings these opportunities were explored and subsequent changes were proposed and are currently being implemented.

Recycling of washout water from sanitising step

The chemical sanitising step in the washout sequence of a storage vessel or mixer was replaced by a hot water sanitising step. It is possible to directly reuse the water coming out of the sanitising step by directing the water back to the CIP tank for reuse. This means that during the sanitising step there should be no effluent water, as the water is constantly flowing back and forth between the CIP tank and mixer. Water at the end of the sanitising step is not discarded, but rather kept in the CIP tank for use in the first step of a washout in a subsequent washout. The basic water flow for the proposed change is shown in Figure 3.

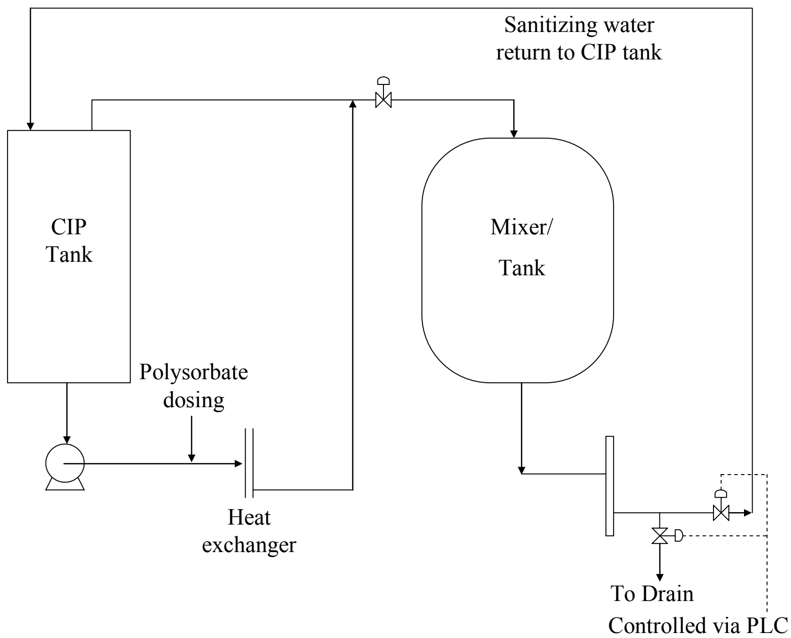

Figure 3. Process flow sheet for the reuse of sanitising water

Table 2 summarizes the savings that should be achieved with the reuse of the sanitising water for two proposed sanitising times. The table gives the amount of water used in each step of a washout. Based on the current washout figures the amount of water saved is 2% of the overall site water usage.

Table 2. Water savings through sanitising water reuse

7 minutes 90°C	
Total other steps	2500 *l*
Sanitising	700 *l*
Total Reused	700 *l*
Savings per washout	**22 %**
30 minutes 82°C	
Total other steps	2500 *l*
Sanitising	3000 *l*
Total Reused	3000 *l*
Water savings per washout	**55 %**

Water for temperature control in the Pharmaceuticals area

The cold water source for both the petroleum jelly (PJ) mixers and the Olsa mixer, in the pharmaceutical mixing area, is municipal water. When it is required to reduce the temperature of the product in any one of the mixers, municipal water is used. The hot water that is currently in circulation is discarded down the drain. The discarded water can be captured by cooling the water and using this water as the cold water supply instead of municipal water.

It is envisaged that the total amount of water saved on site through the installation of cooling towers should be at least 20%. Figure 4 shows the utilities loop and the proposed cooling tower addition.

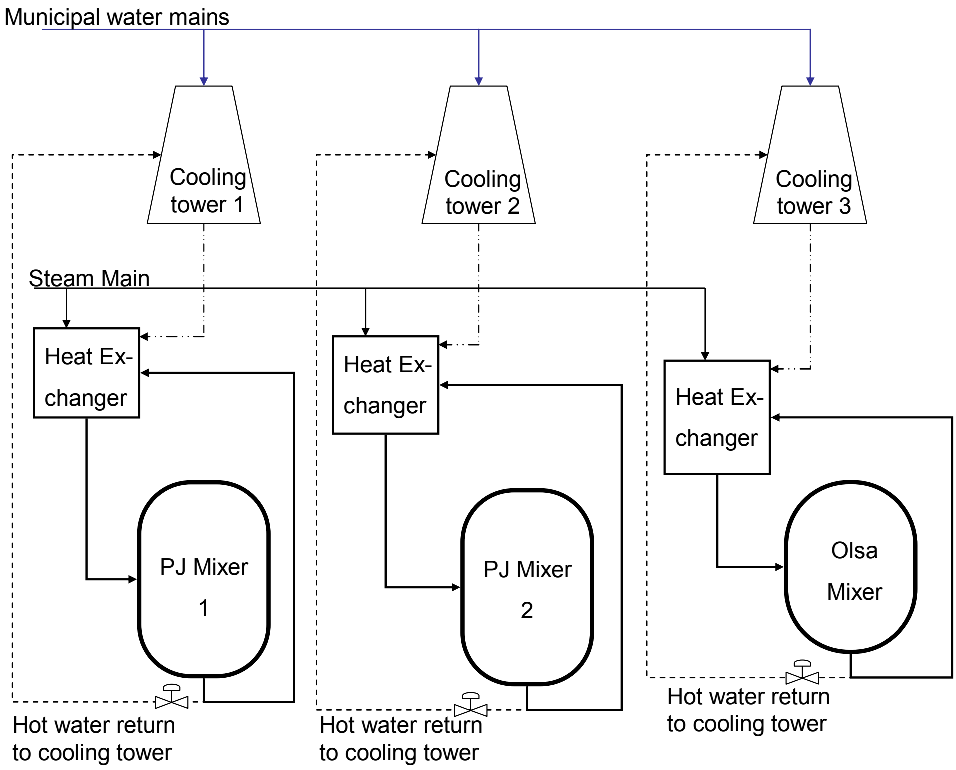

Figure 4. New utilities loop for the PJ and Olsa mixers

Other water saving ideas relating to operational changes

Apart from the two opportunities mentioned above, further opportunities for water savings were also identified. These opportunities would probably not yield as high a savings as the above opportunities, but are worthy of mention. These opportunities are:

- Changing the continuous type washout to a batch washout
- Stationary sprayballs could be changed to the rotary type
- The washout water from an oil phase mixer can be used as a pre-rinse in an aqueous phase
- Reuse of washout water for portable vessel washouts

6. DISCUSSION AND CONCLUSIONS

A wastewater minimisation methodology was successfully used to model an industrial site. The model schedules the production in such a manner as to maximise the amount of water that is reused, thus producing less effluent. The amount of water saved for each washout is dependent on the amount of water used for the sanitising step. The amount of water saved varies between 22% and 55%. The model derived finds practical application as it takes the current water usage into consideration. The output from the model is a production schedule. The production schedule shows the allocation of mixers to various products.

Apart from the model, further water was saved at the industrial site through process related changes. Reusing the sanitising water lead to a 2% savings of the overall water used on site. Capturing the water used for temperature control on the Olsa and PJ mixers at the industrial site leads to 20% savings in the overall water used on site. This is currently being implemented. Further water savings ideas were also identified on the industrial site.

It was observed during the implementation of the wastewater minimisation methodology at the industrial site that the water that was used for the first rinse of a washout contains high levels of product residue and no other contaminants. By changing the type of water used for the first washout from municipal water to deionised water it is very possible to reuse this water as part of the formulation of a batch of a similar product. This would mean that the product residues that would normally be discarded will be recaptured, as is the water from the first washout. This observation would mean that the operation could possibly function in a manner that is tending towards zero effluent. To fully exploit this observation, one would have to derive a methodology that would schedule the operation while reusing water as part of product.

7. RECOMMENDATIONS

It is recommended that future work be done on developing a zero effluent model, since it was observed that pharmaceutical operations generally produce wastewater containing product that can be reused. This then allows any given operation to achieve a near zero discharge scenario. Currently more than 500 tons of product is dispensed with as effluent, which translates to more than R7 million in lost revenue. This is based on 6 batches of product per day with 20 kg residue left per batch, 300 production days per year and the cost of product at R14 per kilogram.

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Mr HM du Plessis	Water Research Commission	(Chairman)
Prof T Majozi	University of Pretoria	(Project Leader)
Prof EMN Chirwa	University of Pretoria	
Ms M Chauke	Dept. Water Affairs and Forestry	
Ms M Mofokeng	Dept. Water Affairs and Forestry	
Mr P Gordon	Sasol Technology (Pty) Ltd	
Prof CA Buckley	University of KwaZulu-Natal	
Dr A Chakraborty	University of Cape Town	
Mr FJ du Toit	Sasol Technology (Pty) Ltd	
Prof T Marwala	University of the Witwatersrand	
Mr B Mokgonyana	Water Research Commission	(Coordinator)

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LIST OF ABBREVIATIONS AND ACRONYMS

CIP	Cleaning in Place
GAMS	General Algebraic Modelling System
LP	Linear program
MIBLP	Mixed integer bilinear program
MILP	Mixed integer linear program
MINLP	Mixed integer non-linear program
MIP	Mixed integer program
NIS	No intermediate storage
NLP	Non-linear program
PJ	Petroleum Jelly
RTN	Resource task network
SA	Simulated annealing
SSN	State sequence network
STN	State task network
UIS	Unlimited intermediate storage
WCA	Water cascade analysis

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1. INTRODUCTION

1.1 Background

Batch processing facilities are a common occurrence in the production of specialty chemicals with high commercial value, more specifically in the production of pharmaceuticals, agrochemicals and fine chemicals. This type of processing is characterized by producing products with similar recipes which facilitates the sharing of processing vessels. These types of processes are discontinuous by nature and hence proper scheduling of the operations is of paramount importance to fully utilize the available equipment.

Increasingly stringent environmental legislation and the high toxicity of the effluents produced from batch processes necessitate the need to minimize the amount of effluent produced from such a facility. The afore mentioned justify the need for an appropriate wastewater minimisation technique. Aqueous effluent produced from a batch process usually stems from liquid-liquid extraction or cleaning of equipment during task changeover. Liquid-liquid extraction is used to extract by-products from a final product using water as the extracting solvent. The cleaning of processing vessels is mandatory in many instances to ensure the integrity of product is not compromised due to cross contamination of products. The aqueous phase from these activities is eventually discarded as effluent.

Most methodologies for wastewater minimisation presented in literature deal with continuous processes at steady state. The main reason for this is that the inherent time dimension of batch processes is not present in continuous processes, which simplifies the methodology. Wastewater minimisation methodologies can be roughly divided into mathematical techniques (El-Halwagi et al., 1992; Doyle and Smith, 1997; Alva-Argáez et al., 1998; Savelski and Bagajewicz, 2000; Jödicke et al., 2001) and graphical techniques (Wang and Smith, 1994, 1995a; Olesen and Polley, 1997; Hallale, 2002). Mathematical techniques have the advantage of being able to deal with multiple contaminant systems, whereas graphical techniques tend to be restricted to single contaminants. Furthermore, mathematical techniques can incorporate process related constraints easier than graphical techniques.

Recently, wastewater minimisation techniques for batch processes have received some attention. Wang and Smith (1995b) adapted their graphical wastewater minimisation technique to batch processes. This technique was solely based on concentration considerations. The technique, however, was more suited to semi-batch, rather than strictly batch processes. Majozi et al. (2006) extended this technique to include strictly batch processes by seeing each water stream as a distinct amount of water available only at a certain time in the time horizon. As with graphical techniques for continuous processes, theses techniques are only applicable to processes involving a single contaminant. Furthermore, the techniques are based on the production schedule being determined beforehand, hence the wastewater target achieved is not necessarily the absolute least amount achievable.

Mathematical techniques are proving to be far superior to graphical techniques since mathematical techniques can deal with the multidimensionality of batch processes. Grau et al. (1996) developed a mathematical technique for waste minimisation with specific emphasis on waste generated during product changeover. The technique is applicable to multi-product facilities and is based on the assumption that there exists an optimal production plan within which the sequence of events is optimized to minimize changeover costs. The methodology is solved using heuristics, which means that the optimality of the solutions obtained be guaranteed. Almató et al. (1997) also developed a wastewater minimisation technique. The technique makes use of storage vessels to overcome time constraints. The optimal tank-to-stream assignment is determined using heuristics. The major limitation of the methodology is that the minimisation was done within a predefined schedule.

Thus far there exists no effective wastewater minimisation technique for batch processes that can be applied to practical situations. A recent case study at a South African agrochemical facility demonstrated an operational cost savings of R800 000 (Majozi, 1998) through wastewater recycle and reuse. The saving was achieved, however, without any formal process integration procedure. The process considered was relatively simple, however, for more complicated processes a formal methodology is required to achieve savings.

1.2 Aims

This project aimed to developed process integration techniques for the minimisation of wastewater in batch processes. Specifically focusing on multipurpose plants characterized by multiple contaminants, since multiple contaminant environments are more common in industry.

1.3 Approach

The proposed techniques will be based on mathematical programming principles, where the overall chemical plant is mathematically modelled. The objective is to maximise profit while minimising effluent. The techniques will find the optimal production schedule, while minimizing wastewater.

The approach adopted in this project entailed mainly 4 stages, i.e. literature review, methodology development, identification of industrial site on which the method had to be tested as well as application of the developed method in a practical environment. A sufficient elaboration on these steps follows.

1.3.1 Literature review

The approach that is generally adopted in the development of the process integration technique is to first undertake a detailed literature review in order to fully understand the subject at hand and gauge the extent of global research. It is through literature review that one gets the opportunity to identify gaps in current research and the limitations of previous methodologies. In the context of this project, the literature review included both scheduling techniques and current wastewater minimisation techniques in batch processes. Understanding current trends in scheduling was deemed paramount in this particular project since it is inherently the basis of any batch process integration technique. (Reported in chapter 2)

1.3.2 Methodology development

Literature review was then followed by the development of the mathematical model embracing both scheduling and wastewater minimization within the same framework. The development of the model was conducted while taking into account the current gaps in research and limitations of current methodologies so as to ensure that the overall methodology addressed the problems at hand. The mathematical model that was developed in this work is based on mathematical programming principles using optimization as an underlying framework. The choice of a mathematical instead of a graphical approach was informed by our understanding of the enormity of the problem at hand. Graphical techniques tend to fail dismally when the size of the problem approaches industrial scale. Moreover, the literature review highlighted a major shortcoming of most published methods, i.e. assuming a predefined schedule prior to wastewater minimization. Our main contribution was to treat both scheduling and wastewater minimisation as optimization problems within a unified framework, which indeed proved more appropriate and optimal than published methods. (Reported in chapter 3)

1.3.3 Industrial site identification

The next stage was the identification of the industrial sites for the application of the methodology. The industrial site of choice would have to be a batch process with significant water utilization and an up to date mass balance. A pharmaceutical site was identified as an ideal facility for the study. Coincidentally, when the investigation started at the beginning of January 2006, the industrial site had just received a corporate mandate to reduce their effluent by more than 10% before the end of 2007. This figure was based on their production at the beginning of the project. Prior to the commencement of this project at the industrial site, more than 60% of water went down the drain, mainly from vessel cleaning and sanitizing. This observation provided an opportunity for achieving the corporate mandate within the prescribed time. (Reported in chapter 4)

1.3.4 Application of the methodology

The final stage was the application of the developed mathematical technique to the chosen industrial site, which is a pharmaceutical production facility as aforementioned. However, prior to applying the technique, full understanding of the process had to be acquired. Consequently, more than 8 months were spent at the facility to ensure close interaction with the personnel, before testing the mathematical model, and another 4 months during the testing of the model. Understanding the process strictly meant informed identification and selection of processes that used enormous amounts of water together with processing parameters and variables that affected daily production schedules. The completed model of the industrial site was then solved using the General Algebraic Modelling System (GAMS) software. Worthy of mention is the fact that it is during this stage that the model was refined to fit the industrial application. (Reported in chapter 5)

1.4. Discussion, conclusion and recommendations

The discussion, conclusion and recommendations are presented in detail in chapters 5 and 6 of this report.

2. LITERATURE REVIEW

2.1 Scheduling in batch processes

Batch processes are especially suited to operations where high value products are produced in low volumes. Such operations are found in pharmaceuticals, fine chemicals, agrochemicals and paint production. Operation of a plant in batch mode is particularly advantageous when many different types of products need to be produced in small volumes, since the same piece of equipment can produce various products.

Batch processing plants can be divided into two main groups based on the path of the products through the plant. The first group is the multiproduct batch plant. Here each product follows the same equipment path through the plant. These plants can produce many different types of products. The second group is the multipurpose batch plant. Products produced in this type of plant do not necessarily follow the same equipment path, i.e. there is no common equipment path through the plant. Plants of this type generally produce products co-currently. This is however not the case of multiproduct batch plants as products are generally processed one at a time (Sparrow et al., 1975).

Due to the discontinuous nature of batch plants scheduling of the operations within the plant is an important task as it has a direct effect on the efficiency and operation of the plant. Scheduling ensures that the optimal arrangement of tasks can be determined so as to obtain the required objective.

The beginning of batch process design and scheduling started with Sparrow et al. (1975) where the authors considered the design of a multiproduct batch plant. In their formulation the timing of the tasks and the time horizon of the operation was taken into account during the optimization of the design. Subsequent design methodologies were proposed by Grossman and Sargent (1979), Knopf et al. (1982), Suhami and Mah (1982), Ravemark and Rippin (1998), which also took scheduling into consideration in some form. The batch process design problem spawned the need for a scheduling framework that effectively made use of all the available equipment.

Kondili et al. (1993) introduced the State Task Network (STN) representation of a process. In the STN representation states are represented by a circle and tasks by a block with an arc joining states to tasks. The STN forms the basis for the sequencing and scheduling formulation proposed by Kondili et al. (1993). The formulation is based on the discrete representation of the time horizon. Here the time horizon is divided into equal length time slots, where the length of the time slot is the highest common factor of the processing times. The starting and ending times of tasks are only allowed to take place within the boundaries of the time slot. A three index binary variable is used to show the start of a task in a certain unit at a certain time. The resulting scheduling formulation takes on the form of a mixed integer linear program (MILP).

The main drawback with the formulation is the number of binary variables. Kondili et al. (1993) note that there could be thousands of binary variables for industrial scale problems. The number of binary variables is in general directly proportional to the computational effort required to solve the problem. Therefore any increase in the number of binary variables increases the computational time. Besides this, the use of the discrete time representation does not necessarily represent the problem accurately as processes with vastly different operating times cannot effectively be represented by a common time slot representation. To deal with this, subsequent scheduling formulations were based on the continuous time representation of the time horizon.

Pinto and Grossmann (1995) proposed a formulation that was based on the continuous time representation of the time horizon. In the formulation the time domain was represented by two parallel coordinates one representing an order (an order representing one batch) and the other a machine. Constraints were derived, based on the number of units in parallel and assignment of orders to machines, to minimise the number of time slots. The resulting formulation was an MILP. The problem noted by Pinto and Grossmann was the large number of binary variables, which reduced the accuracy of the solution and increased the computational time.

Schilling and Pantelides (1996) proposed a formulation based on the resource task network (RTN) representation of a process. In this representation two nodes are considered, namely resource nodes and task nodes. Resource nodes include different materials, such as raw materials, final products, intermediates and storage and transportation equipment. Tasks include processing steps, cleaning, transportation and other operations. The formulation derived by Schilling and Pantelides assumes that tasks only interact with resources at the beginning and ending of an operation.

The formulation is based on the time horizon being divided into a number of time slots of unequal length, i.e. the continuous representation of the time horizon. In the formulation a task begins at the beginning of a time slot and ends at the end of the time slot. A binary variable denotes the usage of a task in a time slot. The formulation took on the form of a MILP.

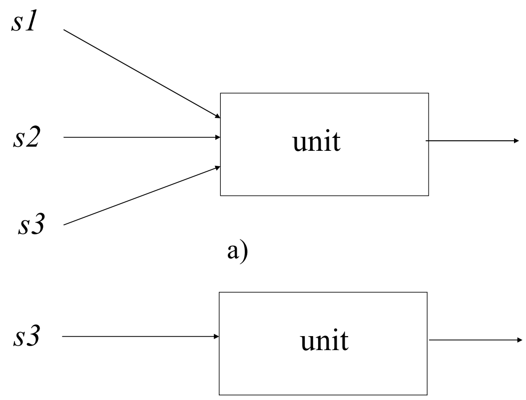
The authors further proposed a novel branch and bound algorithm to solve the formulation. This involves branching on both continuous and binary variables, instead of the traditional binary variable branching. This was done to decrease the solution time of the scheduling model.

Mockus and Reklaitis (1997) proposed a methodology that is also based on the continuous representation of the time horizon. In the formulation variables were introduced to capture the occurrence of an event, e.g. the beginning or ending of a task. The time horizon was divided into unequal time periods with the variables describing the occurrence of an event forming the beginning and ending of the time period. The resulting formulation was a mixed integer non-linear program (MINLP), which was linearised to form a mixed integer bilinear program (MIBLP). The formulation derived by Mockus and Recklaitis used the STN representation of a process.

Following from this, Ierapetritou and Floudas (1998) proposed a scheduling framework using the STN representation. The proposed method had a few novel ideals. The first is the decoupling of tasks and units, this means that the binary variable that originally represented task i in unit j at time p was now represented by two binary variables one representing the usage of a task, i.e. usage of task i at time point p, and one showing the usage of a unit, i.e. usage of unit j at time point p. This meant that the number of binary variables in the formulation decreased from $i \times j \times p$ to $(i \times p)+(j \times p)$. The second idea was the time horizon representation. Ierapetritou and Floudas proposed that the time horizon be represented by a number of event points, where a task begins or ends at an event point. Their subsequent mathematical formulation took the form of a MILP. To find the optimal number of time points in a solution, Ierapetritou and Floudas (1998) proposed that a number of time points be chosen *a priori* and the problem solved, the number of time points is then increased and the problem resolved with the new number of time points. This is done until the objective function reaches a constant value.

Also, using the STN representation and time points, Giannelos and Georgiadis (2002) proposed a framework for scheduling. In the representation a task that can be performed by k distinct units is treated as k distinct tasks, thereby effectively hiding all unit data within the tasks. State task interactions are broken down into three categories, which impact scheduling and the mass balances. The first category deals with states that are consumed by multiple tasks. Here the time at which the state is used for different tasks must be the same, in the event that they are different buffer times ensure they are the same. The second category is where the same state is produced by many tasks. The final category deals with intermediate states and their storage.

Using the time point representation Majozi and Zhu (2001) developed a framework based on the State Sequence Network (SSN) representation of a process. In the SSN representation only states are considered. The change of one state to another implies the usage of a certain task, thus negating the need for binary variables that represent the usage of a task. Furthermore, the method made use of a concept called effective states. An effective state is a state that collectively describes a whole group of states that are used at the same time, by doing this one is reducing the number of binary variables that are used to describe the operation. This can be seen in Figure 1a and 1b. In Figure 1a, 3 states are entering a unit. In this instance an effective state, *s3*, can be defined to collectively describe states *s1*, *s2* and *s3*, as shown in Figure 1b. The methodology derived by Majozi and Zhu took on the form of an MILP that could be solved to global optimality.



b)

Figure 1. Multiple states used by a unit (a) can be described by an effective state (b)

Further work has also been done on scheduling batch processes through constraint based programming (Huang & Chen, 2004) and a combination of MILP and constraint based programming (Maravelias & Grossmann, 2004). The latter has the advantage of being able to reduce the number of constraints and variables that have to be taken into consideration when the final MILP problem is solved. Besides mathematical programming approaches to batch scheduling there have also been approaches based on graph theory.

The S-graph representation is an alternative to the mathematical programming approaches (Holczinger et al., 2002; Sanmartí et al., 2002). In the framework, two types of graphs are depicted, namely a recipe graph and a schedule graph. A node is assigned to each task in a given recipe of a certain product, with a specific node for the product. It is assumed that every task can be performed by at least one of the pieces of equipment that are available. The different task nodes that are involved in the production of a certain product are linked via arcs with a certain weight attached to the arc. The weight of the arc corresponds to the processing time of a certain task within a certain piece of equipment. The resultant graph is called a recipe graph. For multiple batches of the same product the corresponding part of the S-graph is repeated according to the number of batches to get the recipe graph of multiple batches.

The two operating policies that form the basis of the S-graph approach are the unlimited intermediate storage (UIS) policy and the no intermediate storage (NIS) policy. If the UIS policy is followed then the task-nodes that use the same equipment are directly joined with arcs called a schedule arcs. The schedule arcs will show the precedence of tasks in a specific piece of equipment. In the NIS policy, if a piece of equipment is used by a task then a zero weighted arc, or arc whose weight is equal to the change over time, is formed between the task-node after the task-node which uses the piece of equipment and the task-node which uses the piece of equipment next.

Formally the graph is given the form $G(N,A_1,A_2)$ where N, A_1, A_2 denote the sets of nodes, recipe arcs and schedule arcs respectively. A non-negative value is assigned to each arc depicting the time between events. In reality if two nodes are joined then the task at the end of the arc cannot begin earlier than a time c, the weight of the arc, after the starting time of the previous task.

The S-graph approach has been extended to include flexible recipe situations (Romero et al., 2003) and the FIS policy (Romero et al., 2004).

The S-graph solution strategy involves a branch and bound algorithm. What makes the S-graph approach attractive is that problem specific information can be accounted for at the beginning of the optimization. This means that solution times will be reduced. Furthermore, infeasible schedules are identifiable in the early stage of the optimization algorithm, further reducing the computational time. The main drawback of the method is that it is difficult to include other operational policies, even though realistic situations can be modelled by a combination of a NIS and UIS policy (Romero et al., 2004).

Many different approaches have been developed for batch process scheduling with varying degrees of success. Floudas and Lin (2004) provide an in-depth review on scheduling of multipurpose/multiproduct batch plants.

2.2 Wastewater minimisation in continuous processes

Wastewater minimisation in continuous processes has received much attention over the past few years, more than the same subject in batch processes. There are a few reasons for this. The first is that methodologies that deal with continuous processes do not have to deal with time aspect that is inherent in batch processes. In a continuous process water is always flowing continuously and hence there is always water available or needed. Secondly the volume of water produced by continuous processes is generally much higher than in similar batch processes. It has therefore been accepted that saving larger volumes of water is more important than smaller amounts.

Wastewater minimisation methodologies in continuous processes can roughly be divided into graphical techniques (Wang & Smith, 1994,1995a, Olesen & Polley, 1997, Hallale, 2002) and mathematical techniques (Doyle & Smith, 1997; Alva-Argáez, Kokossis & Smith, 1998; Alva-Argáez, Vallianatos & Kokossis, 1999; Zbontar & Glavic, 2000; Liu et al., 2000; Jödicke et al., 2001). The graphical techniques have their roots in cascade analysis and heat pinch. The attractiveness of a graphical technique is the ability of the technique to give the designer insight into the problem and which operations are the constraining operations in terms of water reuse. The disadvantage of graphical methods is that they are unable to deal with multiple contaminants, and depending on the method used can only truly deal with mass transfer based operations.

Mathematical methods have the advantage of being able to deal with multiple contaminants. They have the added advantage of being able to deal with extra constraints such as topographical considerations, forbidden connections, piping constraints and flow rate constraints. Mathematical methods can however result in very large problems that are difficult to solve because of possible non-linearity.

The conditions necessary for a recycle and reuse water network to be optimal were given and proven by Savelski and Bagajewicz (2000). The conditions dealt with referred to the inlet and outlet concentrations of all the operations. Basically the optimal conditions are that the outlet concentration of a unit will not be lower than the combined inlet concentration to the unit and that the inlet and outlet concentrations should be at their maximum.

2.3 Wastewater minimisation in batch processes

Wastewater minimisation in batch processes has not received as much attention as wastewater minimisation in continuous processes. This is because of the discontinuous nature of batch processes and the inherent need to address the discontinuity of the process in any methodology. In a batch process a unit will start operating at a distinct time and end at a distinct time. This means that the need for water and the availability of water for recycle/reuse are at distinct times in the time horizon. Methodologies for wastewater minimisation in batch processes have to take the time dimension into consideration, while still obeying any concentration constraints imposed on the water used for an operation. The methodologies that have been derived thus far for batch processes, as with continuous processes, can be broken into two main groups, namely graphical methods and mathematical methods. Graphical methodologies generally have their roots in established graphical methodologies for wastewater minimisation in continuous processes, whereas mathematical methodologies have their roots in mathematical programming and scheduling of batch processes. The first major developments in wastewater minimisation were based on the graphical approach.

2.3.1 Graphical methods

Wang and Smith (1995b) adopted their Water Pinch method to batch processes. The proposed method is based on the limiting water profile that was developed to deal with wastewater minimisation in continuous processes. Therefore, the method deals with mass transfer based operations.

In batch processes the amount of water used cannot be expressed in units of kilograms per hour, instead it has to be expresses in terms of kilograms. The amount of mass transferred in each operation can be calculated using Equation (1). Here the amount of mass transferred, Δm, is the product of the flowrate of water, f, the change in concentration of the water, ΔC, and the time duration of the water flowrate, Δt. To understand the role of time in batch processes Wang and Smith introduced a variable that describes the quantity of water needed in a batch operation, namely ΔG. The definition of ΔG is given in Equation (2).

$$\Delta m = f \Delta C \Delta t \qquad (1)$$

$$\Delta G = \frac{\Delta m}{\Delta C} = f \Delta t \qquad (2)$$

Using Equation (2), a problem is plotted on a ΔG vs. time axis to give a clearer understanding of the water-using processes in the operation. The graph forms the basis of the water targeting procedure. A problem is divided into time intervals and concentration sub-intervals. The targeting procedure involves determining the water demand for each time interval and concentration interval in the ΔG graph. Within a specific time interval and concentration interval the ΔG graph will be a composite of all the processes operating in that time period at that specified concentration interval. The water demand in a time interval is either made up of reused water or fresh water, depending on what is available in that interval and previous concentration intervals. For each problem the limiting conditions are used to plot the ΔG graph, i.e. the maximum inlet and outlet concentrations respectively. In the method proposed by Wang and Smith, time is taken as the primary constraint and concentration as the secondary constraint, meaning that, in the targeting time constraints are considered before concentration constraints.

The targeting starts with the lowest concentration interval. The water demand for the lowest concentration interval is made up from the fresh water supply. Water from the first concentration interval is then cascaded into higher concentration intervals, while still obeying any time constraints. If there is a deficiency in the amount of water in the higher intervals then it is made up by fresh water. Targeting in this manner also enables one to determine the amount of water that needs to be stored from previous time periods and concentration intervals. Once the targets and storage targets have been identified one can design the network that will achieve the wastewater target.

The methodology proposed by Wang and Smith is based on the schedule known *a priori*. It therefore does not identify the overall least amount of wastewater generation for a certain amount of production. The method is also more suited to semi-continuous processes rather than fully batch processes. Wang and Smith assume that the water is available throughout the time period, which is not the case in true batch processes.

Majozi et al. (2006) extended the methodology of Wang and Smith (1995b) to include strictly batch processes. As with the methodology proposed by Wang and Smith (1995b) the production schedule is determined *a priori*. This means that the water target achieved by the analysis is schedule specific. The methodology is based on the amount of water in each unit being fixed. One of the major features of the methodology is that the inlet concentration of a unit need not be specified, instead the inlet concentration can be found by varying the inlet concentration until the overall water demand does not decrease. This is possible because the water usage within a unit is not determined through concentration considerations as the amount of water is fixed.

The methodology can be implemented in two ways, either by taking time as the primary constraint and concentration as the secondary constraint or taking concentration as the primary constraint and time as the secondary constraint.

Time as the primary constraint

The process starts by dividing the problem into concentration intervals and time subintervals, similar to the procedure described by Wang and Smith (1995b). Boundaries are set by the end-points of each individual processes and then grouping the streams that are available or required in each time interval. This is depicted on a time vs. concentration graph. In a completely batch process it is important to note that water is only required or available at the beginning and the end of a time interval and in discrete amounts. Water available at the end of the time interval can be reused in a subsequent time interval. If there is any surplus at the end of time interval it can either sent to storage or be discarded as effluent. The reuse of water is dependant on the concentration of water. Water at a high concentration cannot be used for operations at a lower concentration but water at a low concentration can be used for operations with a high outlet concentration.

Targeting begins by considering the first concentration interval. Here water required for the process is plotted on a time vs. water demand diagram. As this is the first concentration interval, water that is used is fresh water.

After the first concentration interval the next concentration interval is considered. The analysis of the first concentration interval enables the drawing of the available water profile. The available water profile shows water that has been produced and can be reused within the higher concentration interval. The process water needs in the second concentration profile are depicted on a time vs. water demand graph, as is the available water profile. From this direct reuse possibilities of the wastewater can be seen. If the available water profile is above the demand profile then water reuse can take place. However, if the available water profile goes below the amount of water needed by the process, fresh water is used to makeup the water deficiency. The presence of time gaps between processes and feasible water reuse possibilities show the storage needs.

The targeting continues through each concentration profile. With each new concentration profile, in each concentration interval, the available water profile changes according to the amount of water that has been reused. From the water profiles in each concentration interval one can draw the resulting water reuse network. Important to note is that the concentration requirements are met in each time interval by doing this analysis.

Usually during the plants operation there are units that do not operate within the time horizon and are standing empty. By using this latent storage in the process vessels one is able to reduce the amount of storage needed for the wastewater. To implement the idea the Majozi et al. (2006) propose an inherent storage availability diagram. This diagram depicts each vessels capacity and operation during the time horizon on a capacity vs. time graph. From the graph one is able to see which vessels can store some water while they are standing idle.

Concentration as the primary constraint

The second type of analysis takes concentration as the primary constraint and time as the secondary constraint. The problem is thus split into time intervals and then concentration subintervals. For each time interval each operation is plotted on a concentration vs. water demand graph. For each time interval, each operation will either be labelled as active or complete, to ensure water is reused with accordance to the time constraints.

Operations occurring in the first time interval will be fed by fresh water. In the second and subsequent time intervals water available is cascaded to other units operating within the same time interval or subsequent time intervals. If possible, any surplus water will be transferred to a higher concentration level or stored for use in a later time interval. Water at a certain concentration level cannot be used in a lower concentration level or at an earlier time interval.
One of the main features of taking concentration as the primary constraint is, as each time interval is analysed, so the resulting network is developed. This also enables storage needs to be determined and how the storage will be used within a time horizon.

The methodology by Majozi et al. (2006) suffers as it is mainly developed for fixed water quantity situations. Extending it to situations where the water intake to processes is free to vary and the outlet concentration is fixed is not necessarily possible. Multiple contaminants are not dealt with, as are problems where the schedule is free to change. One of the best points of the methodology is the proposed method to find inherent unit storage opportunities.

Taking a slightly different approach Foo et al. (2005a) derived a graphical method for the synthesis of maximum water recovery for a batch process. This method was based on the methodology derived for the synthesis of a mass exchanger networks by Foo et al. (2004) and Foo et al. (2005b).

The method for water recovery for batch processes proposed by Foo et al. (2005a) determines the water use network that will produce the least amount of wastewater. Semi-continuous and batch processes are considered in the methodology. As with the previous methodologies the schedule is determined *a priori*, hence the target achieved is specific for that schedule. The proposed method is different depending on whether or not there is storage available for the wastewater.

Zero wastewater storage

The first step in the method is to determine the various network targets, i.e. the utility targets, in the respective time intervals. This is then followed by network synthesis.

The time horizon is divided into intervals. In each time interval the respective water demands and sources are determined. A time interval table is introduced to easily determine the sources and sinks (demands) within a time interval. In the time interval table, each stream is located in its specific purity level. The purity of a stream is calculated using Equation (3) (Foo et al., 2005a). Equation (3) relates the concentration of the contaminant to the concentration of pure water, which is 1 000 000 ppm.

$$P = \frac{(1\,000\,000 - C)}{1\,000\,000} \qquad (3)$$

Once the time interval table is set up, water cascade analysis (WCA) is done in each time interval. WCA was originally developed for mass transfer and non-mass transfer water using operations in continuous operations by Manan et al. (2004) but is used in an adapted form in the methodology. The WCA gives the individual utility target for each time interval. The addition of the individual targets for each interval gives the overall utility requirements. In the case with no storage only direct reuse of water is considered, i.e. water is directly reused within a time interval.

Existence of wastewater storage

The use of a dedicated storage vessel for wastewater bypasses, to a certain extent, the inherent time difficulties in batch processes. It should therefore be possible to achieve a larger reduction in the amount of wastewater produced from a process through the use of a storage vessel. The targeting when there is a storage vessel available for wastewater is done using a time dependant WCA.

The first step in the time dependant WCA is to establish the overall utility requirements for the entire network. This then gives the overall fresh water and wastewater flowrates and the global pinch point.

The global pinch that is found in the overall analysis is important as it divides the overall network into two thermodynamic regions. The region above the pinch is the most constrained part of the network and represents a bottleneck for wastewater recovery. The region above the pinch will determine the maximum amount of water that can be recovered. Water sources above the pinch cannot be used for demands below the pinch because of concentration constraints.

After determining the global utility target the individual time interval targets are determined, which is then followed by storage capacity and wastewater flow targeting. The individual fresh water targets are determined in the same manner as when there is no storage available. Water storage is determined by assessing which sinks need water that cannot be satisfied by direct wastewater integration and when the sinks occur in time. The cumulative water storage gives the size of the storage vessel needed for that specific schedule.

Once this analysis has been done, for either case, and the water targets set for each time interval, the water usage network that will achieve the targets is determined. To show the water reuse network, Foo et al. (2005a) introduce a time water network diagram that shows the connections between the various operations as well as their flows in time.

The methodology suffers in that it deals more effectively with semi-continuous processes rather than strictly batch processes. The WCA tool is not suited to discrete batch processes as it is based on water being continuously available. The methodology is also suited to smaller problems. The network design process that is presented gives a network that is only for a specific schedule. Multiple contaminants cannot be taken into account by the method.

The graphical techniques discussed thus far all have common difficulties. They are all based on predefined schedules that make their water targets not necessarily the absolute least amount of wastewater for a given amount of production. They also have an inherent inability to deal with multiple contaminant problems.

Mathematical methodologies were developed to deal with the multi-dimensionality of the batch operations and the wastewater minimisation problem. They have their roots in mathematical programming and optimisation.

2.3.2 Mathematical methodologies

Mathematical methodologies can either be developed to optimise the water usage within a predefined schedule or the methodology can be developed, based on a scheduling methodology, to determine the schedule that will produce the least amount of water. The latter has the advantage of being able to find the absolute least amount of wastewater, depending on the scheduling framework and the objective function.

Wastewater minimisation within a predefined schedule

One of the first methods derived for wastewater minimisation within a predefined schedule was proposed by Almató et al. (1997). The methodology uses storage vessels to overcome the inherent time dimension of batch processes. The methodology seeks to optimise the connections between tanks and operations as to produce the least amount of water. Before the optimisation can take place the direct reuse opportunities are identified in a water stream chart.

Direct reuse is the most desirable situation, due to its inherent simplicity. This, however, cannot always take place due to the timing aspect of the water streams. To overcome this, intermediate storage tanks are used to store water. The stream chart serves as a point to make temporary assignments of streams to tanks. Stream-to-tank and tank-to-process assignments must comply with process concentration constraints, the tanks capacity, the operation concentration constraints and then finally, inherent time constraints.

To find the optimal assignment of tanks-to-water streams, a mathematical model is proposed that describes the tank and operating vessel assignment. This formulation is an NLP and includes tank capacity, stream concentration upper bounds and time constraints. The objective of the mathematical model is to determine which tank will supply which sink and which source will supply which tank so that the amount of fresh water used is minimised. Two fictitious tanks are used to represent the fresh water feed and the wastewater disposal.

To find an initial solution for the NLP a heuristic was developed. The heuristic consists of a sequential tank-stream assignment based on the concentration upper bound. The procedure ensures that filling and concentration constraints are satisfied. This initial solution is used to find the local optimum of the NLP.

Almató et al. (1997) noted that the water target achieved for a certain schedule was not necessarily the absolute minimum. They proposed and algorithm to find the least amount of water usage through sequentially changing the schedule and determining the water target. The algorithm can be computationally intense as the stream chart and optimisation have to be done for each new schedule.

A similar methodology was presented in a later paper by Almató et al. (1999). The main difference came in the solution of the model. In the above paper the authors used simulated annealing and CONOPR to solve the model. Stream temperatures were also taken into account in this methodology, which wasn't the case in the first paper. The methodology was then incorporated into a software package.

Using the similar idea of minimising water within a predefined schedule Kim and Smith (2004) proposed methodology for wastewater minimisation. The aim of the methodology was to minimise the amount of fresh water while maximising the utilisation of equipments and resources.

Before any optimisation takes place the Kim and Smith introduce a limiting water flow profile to give insight into the problem. The limiting water profile gives a limit to the water recovery design, as any design that is below or at the limiting profile is feasible.

The mathematical model derived is based on a superstructure approach. The superstructure represents a unit operation within a time interval. The following features are represented by the superstructure: fresh water is supplied to each operation, wastewater is generated from each operation, re-use of wastewater within the same time interval is allowed, reuse in different time intervals can only be done through a storage vessel, there is a mixer and splitter after each operation and the unit can recycle the wastewater.

The mathematical model derived by Kim and Smith (2004) not only took mass balance constraints and concentration constraints into consideration but also piping cost constraints, storage vessel size constraints and piping network constraints. The objective function is the minimisation of cost where the cost includes the price of the fresh water, the cost of the piping and the cost of the storage tanks.

The resulting model is non-linear as a result of the definition of the inlet and outlet concentrations. Kim and Smith point out that the outlet concentrations tend to their maximum levels, therefore in the single contaminant case the outlet concentration reaches its maximum provided the objective is the minimisation of water only. When there are other considerations, such as piping costs, network costs, etc. this may not be the case. Using the maximum outlet concentration, however, makes the model linear. Using this, Kim and Smith proposed a solution strategy based on an MILP-LP decomposition of the original MINLP problem.

The MILP problem is formulated using the fixed outlet concentrations and slack variables are introduced to compensate for the deviation. The slack variables are incorporated into the original objective function. The values obtained for the water flowrates for the MILP solutions is then used to solve the LP problem. Here the flowrates are fixed and the outlet concentrations are free to change. The objective function of the LP problem is the minimisation of the slack variables. The outlet concentrations achieved from the LP are then used to solve the MILP again. This continues until the either the mass load balance is violated and/or the sum of the slack variables equals zero. Once the solution criteria are satisfied, the values obtained are used as a starting point for the MINLP.

The methodology has the following drawbacks. Firstly the schedule is determined before anything takes place hence the target achieved is schedule specific. Secondly storage is not dealt with effectively enough as superfluous storage is inevitable through the inherent nature of the mathematical formulation. The use of the cost of the piping is also questionable as the contribution of the piping costs could be minimal for a given situation. There are also situations where the use of a pipe is not solely for transferring water hence a restriction on the piping could be a restriction on the transfer of products etc. Lastly, designing a network according to a certain schedule is not practical as the schedule is bound to change.

One of the outstanding features of this methodology, however, is that it does take multiple contaminants into account.

All the methods that minimise water within a predefined schedule have a common problem that the wastewater target achieved might not necessarily be the absolute least amount of wastewater. The absolute least amount of wastewater can only be achieved when the schedule is free to change.

Simultaneous scheduling and wastewater minimization using mathematical modelling

Mathematical formulations that determine the schedule that achieves the absolute least amount of wastewater are generally based on a batch process scheduling framework. The form of the resulting formulation is thus dependant on the scheduling framework on which it is based.

Grau et al. (1996) proposed a scheduling methodology that included wastewater minimisation. The scheduling methodology was based on the continuous time representation of the time horizon where the time horizon was divided into unequal time slots. Each time slot was further divided into subtasks. The subtasks represent all the cleaning, filling and emptying of the vessel and production of the product in the vessel. The advantage of this is that the utility starting and ending times could easily be determined. The wastewater source was mainly product changeover wastewater, i.e. water coming from a cleaning operation during product change over.

A pollution burden was assigned to each wastewater exit stream from the product changeover. This assessed the hazardousness, toxicity and treatment costs of the wastewater. The objective function was to minimise the cost of the product changeover, i.e. minimise the total pollution burden. The model was solved using heuristics and an algorithm developed by Grau et al. (1996).

The main problem with the methodology is that only product changeover wastewater is considered. This is not the only source of wastewater as operations that use water for uses other than cleaning and product changeover also produce wastewater streams. The volumes and toxicity may be higher than that of the product changeover waste. The global optimality of the solution can also not be guaranteed as the method uses heuristics to find a feasible solution.

Recently Majozi (2005a,b) proposed a mathematical method for the minimisation of wastewater in batch processes. This methodology determines the optimum schedule that will produce the least amount of water. The methodology is based on the scheduling framework derived by Majozi & Zhu (2001). A full description of the methodology by Majozi (2005a) is given below.

The first important point of the methodology is the representation of the time horizon. The time horizon in the methodology is based on a time point representation. This is important, as the method of time horizon representation will have a direct effect on the number of binary variables in the formulation.

The mathematical model

Four scenarios are dealt with by Majozi (2005a). The first is where there is a fixed outlet concentration from each unit without central reusable storage. This allows the water used in the operation to vary. The maximum amount of water is the amount of water required when the inlet and outlet concentrations are at their maximums. The second scenario is based on fixed water requirement for each water-using operation without reusable storage. Here the outlet concentration was free to vary, but limited to a maximum by the process. The superstructure used for the derivation of the mathematical model for the first and second scenarios is given in Figure 2.

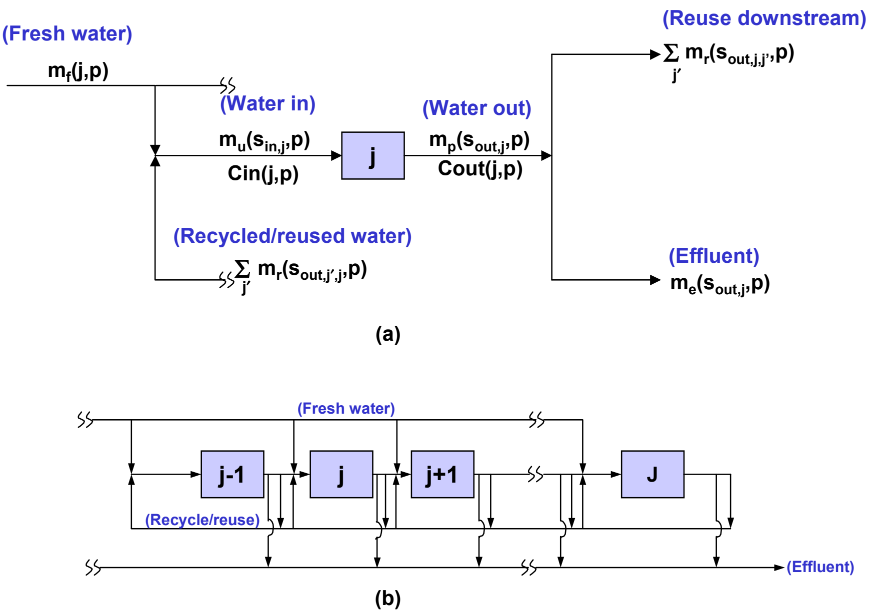


Figure 2. Superstructure used for the first and second scenario showing a unit operation (a) and the overall plant superstructure (b) (Majozi, 2005a)

The third and fourth scenarios are the similar to the first and second; the only difference is that there is central reusable storage for the wastewater. The superstructure used to derive the model for this case is given in Figure 3.

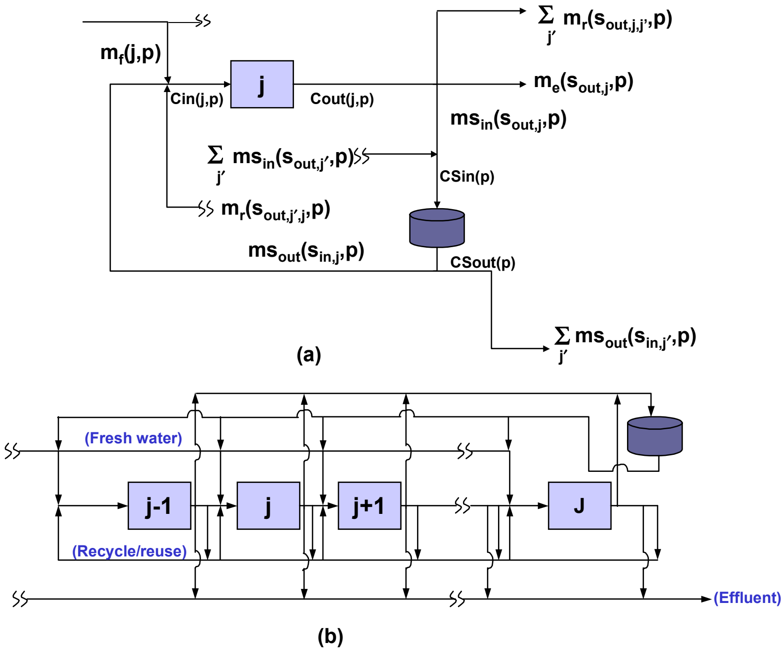


Figure 3. Superstructure for the third and fourth scenarios showing a water using unit and storage (a) and plant overall superstructure (b) (Majozi, 2005a)

During the derivation of the mathematical model by Majozi the following sets, variables and parameters were used

Sets

J = $\{j \mid j \text{ is a unit}\}$

P = $\{p \mid p \text{ is a time point}\}$

$S_{in,j}$ = $\{s_{in,j} \mid s_{in,j} \text{ is an input state to unit } j\}$

$S_{out,j}$ = $\{s_{out,j} \mid s_{out,j} \text{ is an output state to unit } j\}$

$S_{out,j,j'}$ = $\{s_{ou,j,j'} \mid s_{outj,j'} \text{ is a recycle state to unit } j \text{ to unit } j'\}$

S = $\{s \mid s \text{ is state}\} = S_{in,j} \cup S_{out,j} \cup S_{out,j,j'}$

Variables

$C_{out}(j,p)$ = outlet concentration from unit j at time point p

$C_{in}(j,p)$ = inlet concentration to unit j at time point p

$CS_{out}(p)$ = outlet concentration from storage at time point p

$CS_{in}(p)$ = inlet concentration to storage at time point p

$m_e(s,p)$ = amount of state s dispensed with as effluent at time point p,
$s \in S_{out,j}$

$m_f(s,p)$ = amount of fresh water used in unit j at time point p,
$s \in S_{in,j}$

$m_p(s,p)$ = amount of state s produced at time point p,
$s \in S_{out,j}$

$m_u(s,p)$ = amount of state s used at time point p,
$s \in S_{in,j}$

$m_r(s,p)$ = amount of state s recycled or reused between two units j and j' at time point p,
$s \in S_{out,j,j'}$

$ms_{in}(s,p)$ = amount of state s that is transferred to storage at time point p
$s \in S_{out,j}$

$ms_{out}(s,p)$ = amount of state s that is transferred from storage to a particular unit j at time point p,
$s \in S_{in,j}$

$qs(p)$ = amount of water stored at time point p,

$t_p(s,p)$ = time at which state s is produced at time point p,
$s \in S_{out,j}$

$t_r(s,p)$ = time at which state s is recycled or reused between two units j and j' at time point p,
$s \in S_{out,j,j'}$

$t_u(s,p)$ = time at which state s is used at time point p,
$s \in S_{in,j}$

$ts_{in}(s,p)$ = time at which state s is transferred to storage from operation j at time point p,
$s \in S_{out,j}$

$ts_{out}(s,p)$ = time at which state s is transferred to operation j from storage at time point p,
$s \in S_{in,j}$

$y(s,p)$ = binary variable associated with usage of state s at time point p,
$s \in S_{in,j}$

$y_r(s,p)$ =binary variable associated with recycle or reuse between two units j and j' at time point p,
$s \in S_{out,j,j'}$

$ys_{in}(s,p)$ = binary variable associated with the transfer of state s from operation j to storage at time point p,
$s \in S_{out,j}$

$ys_{out}(s,p)$ = binary variable associated with the transfer of state s from

$s \in S_{in,j}$ storage to operation *j* at time point *p*,

Parameters

$\overline{C}_{out}(j)$ = maximum outlet contaminant concentration from unit *j*

$\overline{C}_{in}(j)$ = maximum inlet contaminant concentration to unit *j*

H = time horizon of interest

M(j) = mass-load of contaminant in unit *j*

$\overline{M}_u(j)$ = limiting/maximum water requirement in unit j

$Q_s^0(s)$ = initial amount of state s stored

$\overline{Q}_s$ = maximum capacity of reusable water storage

$\tau(s_{in,j}, p)$ = mean processing time for a state

Scenario 1: fixed outlet concentration without reusable storage

The first constraints considered in the derivation of the mathematical model by Majozi (2005a) are mass balance constraints around a unit. Constraint (4) is a water mass balance into a unit. The inlet stream into any operation comprises of the recycle/reuse streams from all the water using operations and the fresh water stream. The second constraint considered, constraint (5), is an outlet water balance. The outlet stream from any operation can be reused by another process, recycled to the same process or disposed of as effluent. Constraint (6) is a contaminant mass balance around a unit. It simply states that the contaminant mass load difference between the inlet and outlet streams of a unit is the contaminant mass load picked up in that unit. It should be noted that the inlet and outlet stream occur at different time points, the inlet occurs at time point *p-1* and the outlet stream at time point *p*. The inlet concentration is defined in constraint (7). The inlet concentration is merely the ratio between the overall mass load in the recycle and reuse streams and the total amount of water into a unit. The outlet concentration is limited to a predefined maximum by constraint (8). The amount of water cannot exceed the maximum amount of water to a unit. This is enforced by constraint (9).

$$m_u(s_{in,j}, p) = \sum_{s_{out,j',j}} m_r(s_{out,j',j}, p) + m_f(s_{in,j}, p), \qquad (4)$$
$$\forall j, j' \in J, p \in P, s_{in,j} \in S_{in,j}, s_{out,j',j} \in S_{out,j',j}$$

$$m_p\left(s_{out,j},p\right)=m_e\left(s_{out,j},p\right)+\sum_{s_{out,j,j'}} m_r\left(s_{out,j,j'},p\right),$$
$$\forall j,j' \in J, p\in P, s_{out,j}\in S_{out,j}, s_{out,j,j'}\in S_{out,j,j'} \quad (5)$$

$$m_p\left(s_{out,j},p\right)C_{out}(j,p)=m_u\left(s_{in,j},p-1\right)C_{in}(j,p-1) + M(j)y\left(s_{in,j},p-1\right),$$
$$\forall j\in J, s_{in,j}\in S_{in,j}, s_{out,j}\in S_{out,j}, p\in P, p>p_1 \quad (6)$$

$$C_{in}(j,p)=\frac{\sum_{s_{out,j',j}} m_r\left(s_{out,j',j},p\right)C_{out}(j',p)}{\sum_{s_{out,j',j}} m_r\left(s_{out,j',j},p\right)+m_f\left(s_{in,j},p\right)},$$
$$\forall j,j' \in J, p\in P, s_{in,j}\in S_{in,j}, s_{out,j',j}\in S_{out,j',j} \quad (7)$$

$$C_{out}(j,p)=\overline{C}_{out}(j)y\left(s_{in,j},p-1\right), \forall j\in J, p\in P, p>p_1, s_{in,j}\in S_{in,j} \quad (8)$$

$$m_u\left(s_{in,j},p\right)\le \overline{M}_u(j)y\left(s_{in,j},p\right), \forall s_{in,j}\in S_{in,j}, p\in P \quad (9)$$

There are bilinear terms in constraints (6) and (7). The model is thus non-convex and non-linear. To eradicate this, Majozi simplifies these equations through manipulation and substitution and ends up with an equation that contains a bilinear term with a binary variable and a continuous variable. This is then linearised using the Glover (1975) transformation, thus resulting in a linear model.

Scenario 2: fixed water quantity without reusable storage

In this formulation constraints (4)-(7) still hold. However, since the outlet concentration is now free to vary, constraint (8) is modified and the equal sign changes to an inequality sign, as shown in constraint (10). This is similar for constraint (9) where the quantity of water is now fixed and the inequalities sign changes to an equal sign, constraint (11). In this situation there is no opportunity for linearization and hence the model is a MINLP.

$$C_{out}(j,p) \le \overline{C}_{out}(j)\,y(s_{in,j}, p-1),$$
$$\forall j \in J, p \in P, p > p_1, s_{in,j} \in S_{in,j} \tag{10}$$

$$m_u(s_{in,j}, p) = \overline{M}_u(j)\,y(s_{in,j}, p), \forall s_{in,j} \in S_{in,j}, p \in P \tag{11}$$

Scenario 3: fixed outlet concentration and reusable storage

For this scenario constraints (6), (8), and (9) still hold, however, constraints (4), (5) and (7) need to be modified to include water from storage. In this case the inlet water to a unit comprises of water from the central storage unit, water that is recycled or reused and water from the fresh water mains, given in constraint (12). The outlet water from a unit can either be reused or recycled, be sent to the central storage vessel for later use or it can be dispensed as effluent water as shown in constraint (13). The inlet concentration into a unit is not only dependent on the mass load from the recycled/reused water, but also the mass load added from the central storage water. The definition of the inlet concentration is given in constraint (14).

$$m_u(s_{in,j}, p) = \sum_{s_{out,j',j}} m_r(s_{out,j',j}, p) + m_f(s_{in,j}, p) + ms_{out}(s_{in,j}, p),$$
$$\forall j, j' \in J, p \in P, s_{in,j} \in S_{in,j}, s_{out,j',j} \in S_{out,j',j} \tag{12}$$

$$m_p(s_{out,j}, p) = m_e(s_{out,j}, p) + \sum_{s_{out,j,j'}} m_r(s_{out,j,j'}, p) + ms_{in}(s_{out,j}, p),$$
$$\forall j, j' \in J, p \in P, s_{out,j} \in S_{out,j}, s_{out,j,j',p} \in S_{out,j,j'} \tag{13}$$

$$C_{in}(j,p) = \frac{\sum_{s_{out,j',j}} m_r(s_{out,j',j}, p)C_{out}(j',p) + ms_{out}(s_{in,j}, p)CS_{out}(p)}{\sum_{s_{out,j',j}} m_r(s_{out,j',j,}, p) + m_f(s_{in,j}, p) + ms_{out}(s_{in,j}, p)},$$
$$\forall j, j' \in J, p \in P, s_{out,j',j} \in S_{out,j',j}, s_{in,j} \in S_{in,j} \tag{14}$$

Further mass balances are needed in this scenario specifically for the storage vessel. The first is an overall mass water balance around the storage vessel. Here the amount of water stored at a time point is the amount stored in the previous time point and the difference between the inlet and outlet water at that time point, given in constraint (15). This however does not hold for the first time point. Constraint (16) deals with the mass balance at the first time point. It states that the amount of water stored at the first time point is the amount of water initially in the storage vessel and the difference in the inlet and outlet streams. Constraint (17) is added to ensure that the amount of water stored in the storage vessel is within the vessels capacity. A contaminant balance is done on the inlet into the storage vessel. Here the inlet concentration is the ratio of contaminants from water sent from the individual units and the total water sent to the vessel, given in constraint (18). The definition of the concentration inside as well as leaving the vessel is given in constraint (19). It is assumed in this constraint that the storage vessel is ideally mixed and hence the concentration within the vessel is the same as the outlet concentration. The concentration within the vessel is the ratio of the amount of contaminants within the vessel from the previous time point and the amount of contaminants entering the vessel to the amount of water entering the vessel and the amount of water stored in the previous time point. The initial concentration in the storage vessel is given in constraint (20).

$$qs(p) = qs(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j}, p) - \sum_{s_{in,j}} ms_{out}(s_{in,j}, p), \quad \forall j \in J, p \in P, p > p_1, s_{out,j} \in S_{out,j}, s_{in,j} \in S_{in,j} \tag{15}$$

$$qs(p_1) = Q_s^0 - \sum_{s_{in,j}} ms_{out}(s_{in,j}, p_1), \ \forall j \in J, s_{in,j} \in S_{in,j} \tag{16}$$

$$qs(p) \le \overline{Q}_s, \ \forall p \in P \tag{17}$$

$$CS_{in}(p) = \frac{\sum_{s_{out,j}} ms_{in}(s_{out,j})C_{out}(j,p)}{\sum_{s_{out,j}} ms_{in}(s_{out,j}, p)}, \quad \forall j, j' \in J, p \in P, s_{out,j',j} \in S_{out,j',j} \tag{18}$$

$$CS_{out}(p) = \frac{qs(p-1)CS_{out}(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j})C_{out}(j,p)}{qs(p-1) + \sum_{s_{out,j}} ms_{in}(s_{out,j}, p)}, \quad \forall j, j' \in J, p \in P, p > p_1, s_{out,j',j} \in S_{out,j',j} \tag{19}$$

$$CS_{out}(p_1) = CS_{out}^0 \tag{20}$$

The constraints for scenario 3 make the formulation non-convex and non-linear, hence the formulation for this scenario is an MINLP.

Scenario 4: fixed water quantity with reusable central storage

This scenarios mass balance equations consist of constraints 12, 13, 14, 6, 10,11,8,9 and 15-20.

The equations derived above form the mass balance constraints for each scenario. The next step in the mathematical formulation is to consider time.

Sequencing/Scheduling

To ensure that the true nature of batch processes is captured, Majozi (2005a) derived constraints that ensured the correct scheduling of the tasks. Basically, scheduling ensures that water produced at a later time is not falsely allocated to a unit that operates at an earlier time. The scheduling constraints for scenarios one and two are the same. The third and fourth scenarios also have the same scheduling constraints. The main difference in the scheduling between the first two scenarios and the last two scenarios is that the last two scenarios have to take the scheduling of the central storage vessel into consideration.

Sequencing without reusable storage

The first constraints that were taken into consideration for the scheduling deal with the scheduling of recycle and reuse streams. Constraint (21) states that when a unit is receiving water through recycle or reuse the unit starts operating at that time point. However, a unit can start operating at time point p without there being reuse from another unit. Further constraints are developed for recycle and reuse by Majozi (2005a) that ensure the time at which water is recycled/reused coincides with the time at which water is produced and the time at which water is recycled/reused coincides with the time at which a the unit receiving water starts operating, these are not shown here.

$$y_r(s_{out,j,j'}, p) \le y(s_{in,j'}, p), \quad \forall s_{out,j,j'} \in S_{out,j,j'}, s_{in,j'} \in S_{in,j'}, p \in P, j, j' \in J \tag{21}$$

Besides the recycle/reuse scheduling, further scheduling constraints are formulated for the operation of the unit. Here the constraints ensure that the time at which a unit begins to operate is after the unit has finished producing the previous batch and that when a unit starts or ends at two distinct time points, the later time point coincides to a later time.

Scheduling with reusable storage

The first constraints that are dealt with in this section deal with water going into the storage vessel. Here, the time at which water goes to the storage vessel coincides with the ending time of the unit sending the water. This is given in constraints (22) and (23). Constraint (24) ensures that water will only be able to go to storage at time point p provided that the unit sending the water operated in the previous time point. Once again it is not a prerequisite that the when the unit operates it sends water to the storage vessel.

$$ts_{in}\left(s_{out,j},p\right) \geq t_p\left(s_{out,j},p\right) - H\left(1 - ys_{in}\left(s_{out,j},p\right)\right), \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{22}$$

$$ts_{in}\left(s_{out,j},p\right) \leq t_p\left(s_{out,j},p\right) + H\left(1 - ys_{in}\left(s_{out,j},p\right)\right), \quad \forall j \in J, s_{out,j} \in S_{out,j}, p \in P \tag{23}$$

$$ys_{in}\left(s_{out,j},p\right) \leq y\left(s_{in,j},p-1\right), \quad \forall j \in J, s_{in,j} \in S_{in,j}, s_{out,j} \in S_{out,j}, p \in P, p > p_1 \tag{24}$$

Similar constraints were derived for water leaving the storage vessel. The time at which water leaves the storage vessel must coincide with the starting time of the vessel receiving the water, as captured in constraints (25) and (26). Furthermore, water can only go to a unit from storage if that unit is indeed operating at that time point, but a unit can operate without any water being sent to it from storage. This is captured in constraint (27).

$$ts_{out}\left(s_{in,j},p\right) \geq t_u\left(s_{in,j},p\right) - H\left(1 - ys_{out}\left(s_{in,j},p\right)\right), \quad \forall j \in J, s_{in,j} \in S_{in,j}, p \in P \tag{25}$$

$$ts_{out}\left(s_{in,j},p\right) \leq t_u\left(s_{in,j},p\right) + H\left(1 - ys_{out}\left(s_{in,j},p\right)\right), \quad \forall j \in J, s_{in,j} \in S_{in,j}, p \in P \tag{26}$$

$$ys_{out}(s_{in,j}, p) \leq y(s_{in,j}, p), \forall j \in J, s_{in,j} \in S_{in,j}, p \in P \quad (27)$$

Apart from the above scheduling constraints, Majozi (2005a) also derived constraints that ensure that if unit *j* receives water from the storage vessel at a later time point than unit *j'*, then the later time point should correspond to a later time. As well as, constraints that ensure that when two units are receiving water from the storage vessel at a time point the time at which this occurs is the same for both units.

Similar constraints are also formulated to deal with the scheduling of streams entering the storage vessel at different time points and the same time point. Lastly, constraints are also formulated to deal with the scheduling relationship between water streams leaving and entering the vessel at the same time point or earlier time points.

The scheduling constraints that were presented by Majozi (2005a) treated the water using operations as though they were separate from the rest of the batch process. This means that the impact of the other units on the recycle and reuse was not explored. Furthermore, the units that are described by the superstructure approach are for water-using units only and not for units that can perform more than one function, i.e. reactors that can also perform liquid-liquid extraction. The impact of the other units can be easily embedded in a broader scheduling framework. This will then include constraints that encompass the stoichiometry, mass balances, storage, duration, assignment and sequence constraints.

The final part of the mathematical formulation is the objective function. Here Majozi dealt with two types of objective function, either the maximisation of profit or the minimisation of wastewater.

The methodology presented by Majozi (2005a) gave some good results. The superstructure approach makes the application of the methodology to a broad scope of problems. The methodology however does not deal with multiple contaminants and only one storage vessel is considered for wastewater storage.

2.4 Waste Minimisation in Batch Plants

Moving away from strictly wastewater minimisation methodologies Stefanis et al. (1997) proposed a methodology for the combined design of a batch facility while taking waste minimisation into account.

The methodologies aim is to find the cost optimal, structural designs and operating policies of a multipurpose batch plant that minimise the effects of the operation on the environment.

The methodology proposed involves three main steps:

1. definition of batch plant system boundary,
2. aggregated environmental impact assessment and,
3. incorporation of environmental impact criteria in batch plant design and scheduling

A waste vector, defined in the environmental impact, is incorporated into the design and scheduling of the plant to incorporate the environmental effects into the design. The environmental criteria are optimised together with the cost of the design and the scheduling of the batch plant. The environmental effects are weighted by a factor, which can be varied to find a Pareto Curve for the designs.

The formulation is based on a scheduling model where the time horizon was represented by equal length time slots, i.e. the discrete time representation. This means the methodology has inherently many binary variables.

Yao and Yun (1997) followed a similar method to design batch plants with waste minimisation. The approach is divided into three phases namely the production route determination, the production campaign determination and the objective determination, which is based assessment of the environmental impact of waste.

The optimal design of the batch plant is seen as a multi-objective optimisation problem with economic and environmental objectives. The economic objectives are based on the equipment cost, the material cost and the operation cost. The environmental objectives involve the effect of the waste on the environment.

The formulation takes the form of a non-convex MINLP and was solved using a simulated annealing (SA)/LP algorithm. Here the problem is decomposed into two categories: a master program and sub-program. SA is used to solve the master program and LP the sub-program.

As the methodology is done during the grass root design phase scheduling does not have such a pronounced effect in the methodology.

2.5 Conclusion

Both mathematical and graphical techniques exist for the minimisation of wastewater in batch processes. Graphical techniques are limited to single contaminant operations where the schedule is known beforehand. Graphical techniques have the advantage of giving insight into a problem and can identify the processes that are causing bottlenecks in water reuse. Mathematical techniques, however, have the advantage of begin able to determine the wastewater target and schedule that achieves that target simultaneously. Furthermore, mathematical techniques can be extended to multiple contaminant systems and can deal with process related constraints. Mathematical techniques do not give insight into the problem and are therefore a black box type approach.

Past methodologies have not dealt with multiple contaminant systems effectively. Therefore an opportunity exists to develop a multiple contaminant wastewater minimisation methodology. The methodology should determine the wastewater target and schedule that achieves the target simultaneously. Important to note than only if a schedule is free to change can the global minimum wastewater target be achieved. Due to the fact that mathematical techniques are suited to this type of problem the process integration methodologies will be developed based on mathematical programming.

3. MATHEMATICAL MODELS DEVELOPED TO MINIMISE WASTEWATER IN BATCH PROCESSES

From the literature review it was observed that there are very few methodologies that deal specifically with multiple contaminant wastewater minimisation, even though this is more representative of practical situations. Apart from that the methodologies developed thus far are generally based on the schedule being determined beforehand, hence, the wastewater target achieved was not the global minimum. Therefore, what was needed was a mathematical methodology that effectively minimised wastewater within a multiple contaminant environment.

Two mathematical models were developed for this purpose, both dealing with multiple contaminant wastewater minimisation. The first model uses a single storage vessel for wastewater reuse. The second model deals specifically with multiple storage vessels for the wastewater. Both models find application in practical situations. The first model is suited to multiple contaminant wastewater minimisation where there is only one storage vessel available for the storage of wastewater. In these situations there are no restrictions on the type of wastewater that can be stored. The second model finds application to the multiple contaminant environment where there are specific storage requirements that might necessitate the usage of multiple storage vessels. Such situations are found where there are wastewater streams containing different contaminants and these streams should not be mixed. Storage of such streams would then require different storage vessels.

The first methodology for wastewater minimisation with one central storage vessel is described below.

3.1 Multiple Contaminant Wastewater Minimisation

The development of this model was also described elsewhere by Majozi & Gouws (2007)

The problem addressed by the model can be formally stated as:

Given:
i) the contaminant mass load of each contaminant,
ii) the necessary cost and stoichiometric data,
iii) the maximum inlet and outlet concentrations of each contaminant,

iv) the available units and their capacities,
v) the time horizon of interest and
vi) the maximum storage available for water reuse,

determine the production schedule that achieves the minimum amount of wastewater generation through reuse and recycle. Reuse refers to the usage of the outlet water stream from unit *j* in unit *j′* and recycle refers to the usage of the outlet water stream from unit *j* in the same unit *j*..

The proposed mathematical model involves the following sets, variables and parameters.

Sets

$P = \{p \mid p = \text{time point}\}$
$J = \{j \mid j = \text{unit}\}$
$C = \{c \mid c = \text{contaminant}\}$

Variables

$m_{prod}(j,p)$	mass of product produced from unit *j* at time point *p*
$m_{raw}(j,p)$	mass of raw material used in unit *j* at time point *p*
$m_u(j,p)$	mass of water into unit *j* at time point *p*
$m_p(j,p)$	mass water produced at time point *p* from unit *j*
$m_f(j,p)$	mass of fresh water into unit *j* at time point *p*
$me(j,p)$	mass of effluent water from unit *j* at time point *p*
$m_r(j,j',p)$	mass of water recycled to unit *j′* from *j* at time point *p*
$ms_{in}(j,p)$	mass of water to storage from unit *j* at time point *p*
$ms_{out}(j,p)$	mass of water from storage to unit *j* at time point *p*
$C_{in}(j,c,p)$	inlet concentration of contaminant *c*, unit *j,* time point *p*
$C_{out}(j,c,p)$	outlet concentration of contaminant *c*, unit *j,* time point *p*
$CS_{in}(c,p)$	inlet concentration of contaminant *c* into storage at time point *p*
$CS_{out}(c,p)$	outlet concentration of contaminant *c* from storage at time point *p*
$t_u(j,p)$	time that the water is used at time point *p* in unit *j*
$t_p(j,p)$	time at which the water is produced at time point *p* from unit *j*
$t_r(j,j',p)$	time at which water is recycled from unit *j* to unit *j′* at time point *p*

$y(j,p)$	binary variable showing usage of unit j at time point p
$y_r(j,j',p)$	binary variable showing usage of recycle from unit j to unit j' at time point p
$ys_{in}(j,p)$	binary variable showing usage of water into storage from unit j at time point p
$ys_{out}(j,p)$	binary variable showing usage of water from storage to unit j at time point p
$ts_{in}(j,p)$	time at which water goes to storage from unit j at time point p
$ts_{out}(j,p)$	time at which water leaves storage to unit j at time point p

Parameters

$M(j,c)$	mass load of contaminant c added from unit j to the water stream
$\overline{Mu}(j)$	maximum inlet water mass of unit j
$\overline{C}_{in}(c,j)$	maximum inlet concentration of contaminant c in unit j
$\overline{C}_{out}(c,j)$	maximum outlet concentration of contaminant c from unit j
$\tau(j)$	mean processing time of unit j
Q_s^o	initial amount of water stored in the storage vessel
$\overline{Q}_s$	maximum storage capacity of the water storage vessel
$CS_{out}^O(c)$	initial concentration of contaminant c in the storage vessel
$SP(j)$	selling price of product from unit j (c.u./kg product)
$CR(j)$	cost of raw material going into unit j (c.u./kg raw material)
CE	cost of effluent water treatment (cost /kg water)

The mathematical model was derived for two cases. The first case had no central storage vessel for the wastewater. The second case did have a central storage vessel for wastewater.

3.1.1 Wastewater minimisation without storage

The mathematical formulation for the case where there is recycle and reuse of wastewater without intermediate storage is based on the superstructure given in Figure 4 (Majozi, 2005a). Figure 4a represents a single water using unit and Figure 4b shows the broader plant superstructure. The distinction between Figs 3 and 4 should be noted.

In Figure 4a, for each water-using operation water into the unit is a combination of the freshwater and water recycled from other units to that unit. Water leaving the unit can either be discarded as effluent or be recycled /reused in other units.

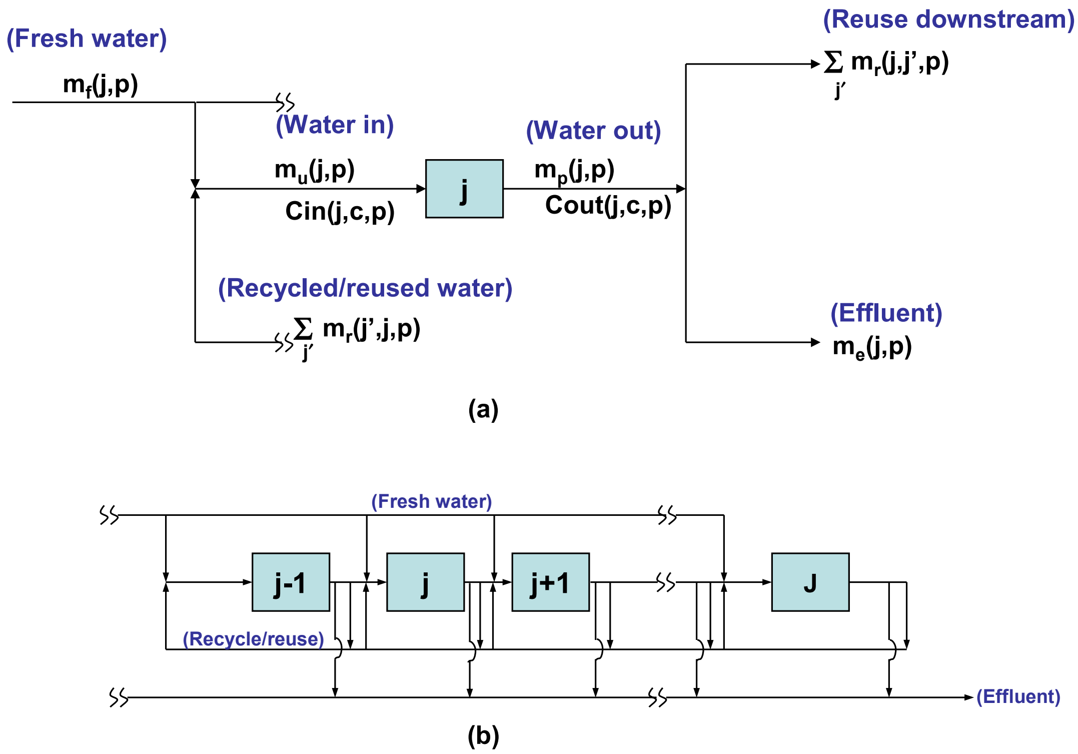


Figure 4. Superstructure used for a water using unit (a) and overall plant superstructure (b) for the case with no storage

Mass balance constraints

The first constraints considered are the mass balance constraints. A mass balance is done over the inlet into a unit, over the outlet of the unit and over the unit itself. Constraint (28) is a water balance over the inlet to a unit. The total water into a unit is the sum of all water recycled to the unit and the fresh water into the unit. It is assumed that the operation that takes place in a unit does not produce water as captured in constraint (29). Constraint (30) is an outlet water balance from a unit. Here the total water out of a unit is the sum of all the recycle streams to other units and the water discarded as effluent. Constraint (31) is a contaminant balance over a unit. It is also the definition if the outlet concentration. The mass of contaminants out of a unit is the sum of the contaminants into the unit and the mass of contaminants added from the operation performed in the unit. As there is more than one contaminant present in the system the balance has to be done for each contaminant. Constraint (32) is the definition of the inlet concentration of a contaminant in a unit. The inlet concentration is defined as the mass of contaminants from the recycle streams divided by the total water into a unit.

$$m_u(j,p) = \sum_{j'} m_r(j',j,p) + m_f(j,p), \quad \forall j, j' \in J, p \in P \tag{28}$$

$$m_u(j,p-1) = m_p(j,p), \quad \forall j \in J, p \in P \tag{29}$$

$$m_p(j,p) = m_e(j,p) + \sum_{j'} m_r(j,j'p), \quad \forall j, j' \in J, p \in P \tag{30}$$

$$\begin{aligned} m_p(j,p)C_{out}(j,c,p) = m_u(j,p-1)C_{in}(j,c,p-1) + M(j,c)y(j,p-1), \\ \forall j \in J, p \in P, p > p_1, c \in C \end{aligned} \tag{31}$$

$$\begin{aligned} C_{in}(j,c,p) = \frac{\sum_{j'} m_r(j',j,p)C_{out}(j',c,p)}{\sum_{j'} m_r(j',j,p) + m_f(j,p)}, \\ \forall j, j' \in J, p \in P, c \in C \end{aligned} \tag{32}$$

The outlet concentration of each contaminant in a unit cannot exceed its maximum limit as stated in constraint (33). Constraint (34) ensures that the total water into a unit does not exceed the maximum allowable for that unit. Constraint (35) restricts the mass of water recycled into a unit to the maximum allowable water for that unit. Constraint (36) stipulates that the inlet concentration for a contaminant into a unit cannot exceed its upper limit.

$$C_{out}(j,c,p) \leq \overline{C}_{out}(c,j)y(j,p-1), \forall j \in J, p \in P, p > p_1, c \in C \tag{33}$$

$$m_u(j,p) \leq \overline{M}_u(j)y(j,p), \forall s_{in,j} \in S_{in,j}, p \in P \tag{34}$$

$$m_r(j',j,p) \leq \overline{M}_u(j)y_r(j',j,p), \forall j, j' \in J, p \in P \tag{35}$$

$$C_{in}(j,c,p) \leq \overline{C}_{in}(c,j)y(j,p), \forall j, j' \in J, p \in P, c \in C \tag{36}$$

The maximum water quantity into a unit is represented by Equation (37). It is important to note that for multi-contaminant wastewater the outlet concentrations 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.

$$\overline{M}_u(j) = \max_{c \in C} \left\{ \frac{M(j,c)}{\overline{C}_{out}(j,c) - \overline{C}_{in}(j,c)} \right\}, \quad \forall\ j \in J \tag{37}$$

Due to the discontinuous nature of batch processes the mass balances are not enough to fully describe the system. Sequencing constraints need to capture the discontinuous nature of the operation.

Recycle/Reuse sequencing constraints

Scheduling of the recycle/reuse streams is important because of the discontinuous manner of the streams existence. The first constraint considered is constraint (38). This constraint stipulates that recycle/reuse between units can only take place when the unit receiving the wastewater is operating at that time point. The unit receiving the wastewater, however, does not need to receive wastewater to operate, i.e. it can operate independent of the wastewater recycle/reuse. Constraints (39) and (40) ensure that the time at which recycle/reuse of water takes place is the same time as that at which water is produced. Constraints (41) and (42) ensure that the starting time of the unit receiving water coincides with the time at which that water is recycled/reused.

$$y_r(j,j',p) \le y(j',p), \quad \forall\ p \in P, j, j' \in J \tag{38}$$

$$t_r(j,j',p) \le t_p(j,p) + H\left(1 - y_r(j,j',p)\right), \quad \forall\ j, j' \in J, p \in P \tag{39}$$

$$t_r(j,j',p) \ge t_p(j,p) - H\left(1 - y_r(j,j',p)\right), \quad \forall\ j, j' \in J, p \in P \tag{40}$$

$$t_r(j,j',p) \le t_u(j',p) + H\left(1 - y_r(j,j',p)\right), \quad \forall j,j' \in J, p \in P \tag{41}$$

$$t_r(j,j',p) \ge t_u(j',p) - H\left(1 - y_r(j,j',p)\right), \quad \forall j,j' \in J, p \in P \tag{42}$$

Task scheduling constraints

Each task in the time horizon has to be scheduled. This is captured in Equations (43)-(45). Constraint (43) states that a unit is only allowed to operate once the unit has finished the previous operation. Constraint (44) and constraint (45) ensure that each time a unit begins or ends it does so at a later time with each respective time point.

$$t_u(j,p) \ge t_p(j,p) - H\left(2 - y(j,p) - y(j,p-1)\right), \quad \forall j \in J, p \in P, p > p_1 \tag{43}$$

$$t_u(j,p) \ge t_u(j,p') - H\left(2 - y(j,p) - y(j,p')\right), \quad \forall j \in J, p, p' \in P, p \ge p' \tag{44}$$

$$t_p(j,p) \ge t_p(j,p') - H\left(2 - y(j,p) - y(j,p')\right), \quad \forall j \in J, p, p' \in P, p \ge p' \tag{45}$$

Feasibility constraints

Constraint (46) is added to the formulation to ensure that two units do not recycle to each other at the same time point, i.e. if unit j recycles to unit j', unit j' may not recycle to unit j.

$$y_r(j,j',p) + y_r(j',j,p) \le 1, \qquad \forall j,j' \in J, p \in P \tag{46}$$

Linearization

Constraints (31) and (32) contain bilinear terms. This makes the model nonlinear. The terms can be linearised according to the linearization of bilinear terms proposed by Quesada and Grossman (1995). The linearization is as follows:

Let:

$$C_{in}(j,c,p)m_u(j,p) = \Gamma_1(j,c,p)$$
$$C_{out}(j,c,p)m_p(j,p) = \Gamma_2(j,c,p)$$
$$C_{out}(j',c,p)m_r(j',j,p) = \Gamma_3(j',j,c,p),$$

with each variable having the following bounds

$$0 \le C_{in}(j,c,p) \le \overline{C}_{in}(j,c)$$
$$0 \le M_u(j,p) \le \overline{M}_u(j)$$
$$0 \le C_{out}(j,c,p) \le \overline{C}_{out}(j,c)$$
$$0 \le M_p(j,p) \le \overline{M}_u(j)$$
$$0 \le M_r(j',j,p) \le \overline{M}_u(j'),$$

then the following constraints are true for Γ_1

$$\Gamma_1(j,c,p) \ge 0, \forall j \in J, p \in P, c \in C \tag{47}$$

$$\Gamma_1(j,c,p) \ge \overline{M}_u(j)C_{in}(j,c,p) + \overline{C}_{in}(j,c)m_u(j,c,p) - \overline{M}_u(j)\overline{C}_{in}(j,c)), \quad \forall j \in J, p \in P, c \in C \tag{48}$$

$$\Gamma_1(j,c,p) \le \overline{M}_u(j)Cin(j,c,p), \quad \forall j \in J, p \in P, c \in C \tag{49}$$

$$\Gamma_1(j,c,p) \le m_u(j,p)\overline{C}_{in}(j,c), \quad \forall j \in J, p \in P, c \in C, \tag{50}$$

and the following constraints for Γ_2

$$\Gamma_2(j,c,p) \ge 0, \quad \forall j \in J, p \in P, c \in C \tag{51}$$

$$\Gamma_2(j,c,p) \ge \overline{M}_u(j)C_{out}(j,c,p) + \overline{C}_{out}(j,c)m_p(j,c,p) - \overline{M}_u(j)\overline{C}_{out}(j,c)), \quad \forall j \in J, p \in P, c \in C \tag{52}$$

$$\Gamma_2(j,c,p) \le \overline{M}_u(j)C_{out}(j,c,p), \quad \forall j \in J, p \in P, c \in C \tag{53}$$

$$\Gamma_2(j,c,p) \le m_p(j,p)\overline{C}_{out}(j,c), \quad \forall j \in J, p \in P, c \in C, \tag{54}$$

and the following constraints for Γ_3

$$\Gamma_3(j',j,c,p) \geq 0, \quad \forall j,j' \in J, p \in P, c \in C \tag{55}$$

$$\Gamma_3(j',j,c,p) \geq \overline{M}_u(j)C_{out}(j',c,p) + \overline{C}_{out}(j',c)m_r(j',j,c,p) - \overline{M}_u(j)\overline{C}_{out}(j',c), \\ \forall j,j' \in J, p \in P, c \in C \tag{56}$$

$$\Gamma_3(j',j,c,p) \leq \overline{M}_u(j)C_{out}(j',c,p), \quad \forall j,j' \in J, p \in P, c \in C \tag{57}$$

$$\Gamma_3(j',j,c,p) \leq m_r(j',j,p)\overline{C}_{out}(j',c), \quad \forall j,j' \in J, p \in P, c \in C. \tag{58}$$

Substituting the above linearised variables into constrains (31) and (32) give constraints (59) and (60).

$$\Gamma_1(j,c,p) = \sum_{j'} \Gamma_3(j',j,c,p), \quad \forall j,j' \in J, p \in P, c \in C \tag{59}$$

$$\Gamma_2(j,c,p) = \Gamma_1(j,c,p-1) + M(j,c)y(j,p-1), \quad \forall j \in J, p \in P, c \in C \tag{60}$$

3.1.2 Wastewater minimisation with central storage

The formulation of the model with storage is based on the superstructure given in Figure 5. Figure 5a represents a single water using unit and Figure 5b represents the overall plant superstructure. For a unit, represented in Figure 5a, the total water flowing into the unit in this instance is the sum of the fresh water, the water recycled/reused from the other units and the water from storage. The water leaving the unit is then the sum of the water going to effluent, the water going to storage and the water being reused/recycled.

Mass balance constraints

Constraints (28), (30) and (32) need to be modified to cater for the water from storage, thus yielding constraints (61), (62) and (63). The difference between constraint (28) and constraint (61) is that water into the unit is not only water from recycle and fresh water, but water from storage as well. This is similar for constraint (62) where outlet water involves recycled water, water that goes to effluent and water that goes to storage. The inlet concentration is not only affected by the contaminants from the recycle as in the previous case, but also the contaminants in the water from the storage tank as stated in constraint (63).

$$m_u(j,p) = \sum_{j'} m_r(j',j,p) + mf(j,p) + ms_{out}(j,p), \quad \forall j,j' \in J, p \in P \tag{61}$$

$$m_p(j,p) = \sum_{j'} m_r(j,j',p) + me(j,p) + ms_{in}(j,p), \quad \forall j,j' \in J, p \in P \tag{62}$$

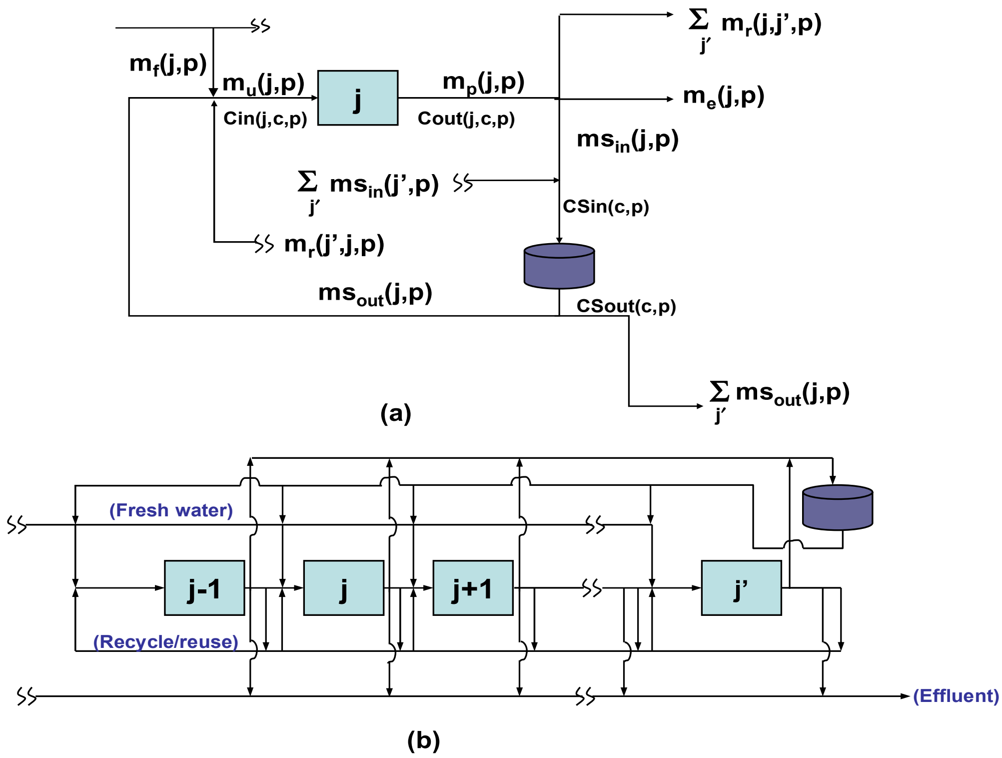


Figure 5. Superstructure for a water using unit (a) and overall plant (b) for the model with reusable storage

$$C_{in}(j,c,p)m_u(j,p) = \sum_{j'} m_r(j',j,p)C_{out}(j',c,p) + ms_{out}(j,p)Cs_{out}(c,p),$$
$$\forall j, j' \in J, p \in P, c \in C \tag{63}$$

In the case where there was no storage for the wastewater all the bilinear terms in Equation (31) were linearised yielding a new linear equation. This linearization, however, is not possible for the case where there is water storage. However, it is worth mentioning that the only term that presented difficulties during model solution was $C_{out}(c,j,p)m_p(j,p)$ and its linearization is exactly the same as that given in Equations (51)-(54). Substituting the linearization discussed previously into Equation (31) then yields Equation (64).

$$\Gamma_2(j,c,p) = C_{in}(j,c,p-1)m_u(j,p-1) + M(j,c)y(j,p-1),$$
$$\forall j \in J, p \in P, c \in C, p > p_1 \tag{64}$$

Besides the mass balances over the water using operation, there also has to be mass balances over the storage unit. Constraint (65) is a water balance over the storage unit. The water in the storage vessel at a certain time point is the difference between the water flowing into and from the storage vessel and the water possibly stored from a previous time point. Constraint (66) is a water mass balance at the beginning of the time horizon. At the beginning of the time horizon there is no water flowing into the vessel, but there might be an initial amount of water in the vessel and hence there might be water leaving the vessel. Constraint (67) ensures that the storage in the vessel does not exceed the vessels storage capacity. Constraint (68) is the definition of the inlet concentration into the storage vessel and constraint (69) is the definition of the outlet concentration from the vessel. It should be noted that constraint (70) is based on the assumption that the contaminant concentration inside the storage unit is the same as the concentration of the exit stream. Constraint (71) is the initial concentration of water in the storage tank at the beginning of the time horizon, provided there is an initial amount of water in the storage tank. Constraint (72) ensures that water flowing from storage to a unit does not exceed the unit's capacity.

$$qs(p) = qs(p-1) + \sum_j ms_{in}(j,p) - \sum_j ms_{out}(j,p), \quad \forall j \in J, p \in P, p > p_1 \tag{65}$$

$$qs(p_1) = Q_s^0 - \sum_j ms_{out}(j,p_1), \ \forall j \in J \tag{66}$$

$$qs(p) \leq \overline{Q}_s, \ \forall p \in P \tag{67}$$

$$CS_{in}(c,p) = \frac{\sum_j (ms_{in}(j,p) C_{out}(j,c,p))}{\sum_j ms_{in}(j,p)}, \quad \forall j, j' \in J, p \in P, c \in C \tag{68}$$

$$CS_{out}(c,p) = \frac{qs(p-1) CS_{out}(c,p-1) + \left(\sum_j ms_{in}(j,p) \right) CS_{in}(c,p)}{qs(p-1) + \sum_j ms_{in}(j,p)}, \quad \forall j, j' \in J, p \in P, p > p_1, c \in C \tag{69}$$

$$CS_{out}(c,p_1) = CS_{out}^0(c), \quad \forall\, c \in C \tag{70}$$

$$ms_{out}(j,p) \leq \overline{M}_u(j) ys_{out}(j,p), \quad \forall j, j' \in J, p \in P \tag{71}$$

Sequencing constraints associated with storage

Constraints (72) and (73) ensure that the time at which wastewater is produced from a vessel is the same time at which the wastewater is transferred to storage. Furthermore, wastewater can only be sent to storage if the unit which produced the wastewater has operated. However the fact that a unit has operated does not mean that water needs to be sent to storage from that unit. This is captured in constraint (74)

$$ts_{in}(j,p) \geq t_p(j,p) - H\left(1 - ys_{in}(j,p)\right), \quad \forall j \in J, p \in P \tag{72}$$

$$ts_{in}(j,p) \leq t_p(j,p) + H\left(1 - ys_{in}(j,p)\right), \quad \forall j \in J, p \in P \tag{73}$$

$$ys_{in}(j,p) \leq y(j,p-1), \quad \forall j \in J, p \in P, p > p_1 \tag{74}$$

Constraints (75) and (76) ensure that the time at which wastewater goes from storage to a unit is the same time at which that unit starts its operation. Constraint (77) ensures that the unit is indeed operating when the unit is using wastewater from storage. The unit, however, does not necessarily have to use water from storage when it operates. A unit will not use the water in storage if there is a violation of the inlet concentration of the water into the unit or if there is simply no water in the storage vessel.

$$ts_{out}(j,p) \geq t_u(j,p) - H\left(1 - ys_{out}(j,p)\right), \quad \forall j \in J, p \in P \tag{75}$$

$$ts_{out}(j,p) \leq t_u(j,p) + H\left(1 - ys_{out}(j,p)\right), \quad \forall j \in J, p \in P \tag{76}$$

$$ys_{out}(j,p) \leq y(j,p), \quad \forall j \in J, p \in P \tag{77}$$

Constraint (78) ensures that when water is transferred to a unit at a time point, the time at which this happens is later in the time horizon than any previous time water was transferred to other units at previous time points. Constraints (79) and (80) ensure that the time at which wastewater is moved from storage to different units at the same time point is the same time, i.e. all the water leaving the storage tank at a time point leaves at the same time.

$$ts_{out}(j,p) > ts_{out}(j',p') - H\left(2 - ys_{out}(j,p) - ys_{out}(j',p')\right), \quad \forall j,j' \in J, p,p' \in P, p > p' \tag{78}$$

$$ts_{out}(j,p) \geq ts_{out}(j',p) - H\left(2 - ys_{out}(j,p) - ys_{out}(j',p)\right), \quad \forall j,j' \in J, p \in P \tag{79}$$

$$ts_{out}(j,p) \leq ts_{out}(j',p) + H\left(2 - ys_{out}(j,p) - ys_{out}(j',p)\right), \quad \forall j,j' \in J, p \in P \tag{80}$$

Constraint (81) is similar to constraint (78), but it applies to inlet streams to the storage tank. Constraints (82) and (83) ensure that the time at which there is wastewater going to storage from two different units corresponds to the same time at a time point.

$$ts_{in}(j,p) > ts_{in}(j',p') - H\left(2 - ys_{in}(j,p) - ys_{in}(j',p')\right), \quad \forall j,j' \in J, p,p' \in P, p > p' \tag{81}$$

$$ts_{in}(j,p) \geq ts_{in}(j',p) - H\left(2 - ys_{in}(j,p) - ys_{in}(j',p)\right), \quad \forall j,j' \in J, \in S_{out,j}, p \in P \tag{82}$$

$$ts_{in}(j,p) \leq ts_{in}(j',p) + H\left(2 - ys_{in}(j,p) - ys_{in}(j',p)\right), \quad \forall j,j' \in J, p \in P \tag{83}$$

Constraint (84) ensures that the outlet time of water from storage tank at a time point occurs later than the inlet time at previous time points. Constraints (85) and (86) ensure that at a time point the time at which water is moved to storage is the same as the time at which water leaves the storage.

$$ts_{out}(j,p) > ts_{in}(j',p') - H\left(2 - ys_{out}(j,p) - ys_{in}(j',p')\right), \quad \forall j,j' \in J, p,p' \in P, p > p' \tag{84}$$

$$ts_{out}(j,p) \geq ts_{in}(j',p) - H\left(2 - ys_{out}(j,p) - ys_{in}(j',p)\right), \quad \forall j,j' \in J, p \in P \tag{85}$$

$$ts_{out}(j,p) \leq ts_{in}(j',p) + H\left(2 - ys_{out}(j,p) - ys_{in}(j',p)\right), \quad \forall j,j' \in J, p \in P \tag{86}$$

The following constraints ensure that all the water reuse and recycle opportunities are explored within the time horizon of interest.

$$ts_{in}(j,p) \leq H, \quad \forall j \in J, p \in P \tag{87}$$

$$ts_{out}(j,p) \leq H, \quad \forall j \in J, p \in P \tag{88}$$

$$t_u(j,p) \leq H, \quad \forall j \in J, p \in P \tag{89}$$

$$t_p(j,p) \leq H, \quad \forall j \in J, p \in P \tag{90}$$

$$t_r(j,j',p) \leq H, \quad \forall j,j' \in J, p \in P \tag{91}$$

Objective Function

The objective function is the maximisation of profit, where profit is the difference between the revenue derived from product, the cost of the raw materials and the treatment costs of the effluent water. This is given in constraint (92)

$$max\ R = \sum_p \left(\sum_j SP(j) m_{prod}(j,p) - \sum_j CR(j) m_{raw}(j,p) - CE \sum_j me(j,p) \right), \quad \forall j \in J, p \in P \tag{92}$$

The second model developed deals with multiple contaminant wastewater minimisation with multiple storage vessels for the wastewater.

3.2 Multiple Contaminant Wastewater Minimisation with Multiple Storage Vessels

The problem to be solved, stated formally, is:

Given:

i) the contaminant mass load of each contaminant,

ii) the necessary cost and stoichiometric data,

iii) the maximum inlet and outlet concentrations of each contaminant to each unit,

iv) the number of storage vessels and their maximum inlet concentration of each contaminant into the vessel,

v) the available units and their capacities,

vi) the time horizon of interest, and

vii) the maximum capacity of storage available for water reuse,

determine the production schedule that achieves the minimum amount of wastewater generation through reuse and recycle and use of the available storage opportunities.

The following sets, variables and parameters are used in the methodology.

Sets

$P = \{p \mid p = \text{time point}\}$

$J = \{j \mid j = \text{unit}\}$

$C = \{c \mid c = \text{contaminant}\}$

$U = \{u \mid u = \text{reusable water storage vessel}\}$

Variables

$F_u(j,p)$	mass of water into unit j at time point p
$F_p(j,p)$	mass water produced at time point p from unit j
$F_e(j,p)$	mass of fresh water into unit j at time point p
$F_f(j,p)$	mass of effluent water from unit j at time point p

$F_r(j',j,p)$	mass of water recycled to unit *j* from *j'* at time point *p*
$Fs_{in}(j,u,p)$	mass of water to storage vessel *u* from unit *j* at time point *p*
$Fs_{out}(u,j,p)$	mass of water from storage vessel *u* to unit *j* at time point *p*
$C_{in}(j,c,p)$	inlet concentration of contaminant *c* of unit *j* at time point *p*
$C_{out}(j,c,p)$	outlet concentration of contaminant *c* of unit *j* at time point *p*
$Cs_{in}(u,c,p)$	inlet concentration of contaminant *c* into storage vessel *u* at time point *p*
$Cs_{out}(u,c,p)$	outlet concentration of contaminant *c* from storage vessel *u* at time point *p*
$m_u(s_{in},j,p)$	mass of raw material used in unit *j* at time point *p*
$m_p(s_{out},j,p)$	mass of product produced from unit *j* at time point *p*
$t_u(s_{in},j,p)$	time that the water is used at time point *p* in unit *j*
$t_p(s_{out},j,p)$	time at which the water is produced at time point *p* from unit *j*
$t_r(j',j,p)$	time at which water is recycled from unit *j* to unit *j'* at time point *p*
$ts_{in}(j,u,p)$	time at which water goes to storage vessel *u* from unit *j* at time point *p*
$ts_{out}(u,j,p)$	time at which water leaves storage vessel *u* to unit *j* at time point
$y(s_{in},j,p)$	binary variable for usage of unit *j* at time point *p*
$y_r(j',j,p)$	binary variable for usage of recycle from unit *j* to unit *j'* at time point *p*
$ys_{in}(j,u,p)$	binary variable for usage of water into storage vessel *u* from unit *j* at time point *p*
$ys_{out}(u,j,p)$	binary variable for usage of water from storage vessel *u* to unit *j* at time point *p*

Parameters

$SP(s_{out})$	selling price of product from unit *j* (c.u./kg product)
$CR(s_{in})$	cost of raw material going into unit *j* (c.u./kg raw material)
CE	cost of effluent water treatment (cost /kg water)
$M_{lost}(c,j)$	mass load of contaminant *c* added from unit *j* to the water stream
$\overline{F}_w(j)$	maximum amount of water to unit *j*
$\overline{C}_{in}(c,j)$	maximum inlet concentration of contaminant *c* in unit *j*
$\overline{C}_{out}(c,j)$	maximum outlet concentration of contaminant *c* from unit *j*
$\tau(j)$	mean processing time of unit *j*

Q_s^o	initial amount of water stored in the storage vessel
$\overline{Q}_s$	maximum storage capacity of the water storage vessel
$CS_{out}^{O}(c,u)$	initial concentration of contaminant c in the storage vessel u
$\overline{C}s_{in}(c,u)$	maximum inlet concentration of contaminant c into storage vessel u

Superstructure used

The superstructure used in the derivation of the model is given in Figure 6. Figure 6a represents a water using unit within an operation. In Figure 6a it can be seen that water used by a unit is made up of water that is recycled/reused directly, fresh water and water reused from the storage vessels. This is similar for the water leaving the unit, where this water is either recycled/reused to other units directly, discarded as effluent or sent to a storage vessel for reuse at a later stage. Figure 6b shows the overall plant superstructure that each unit forms a part of.

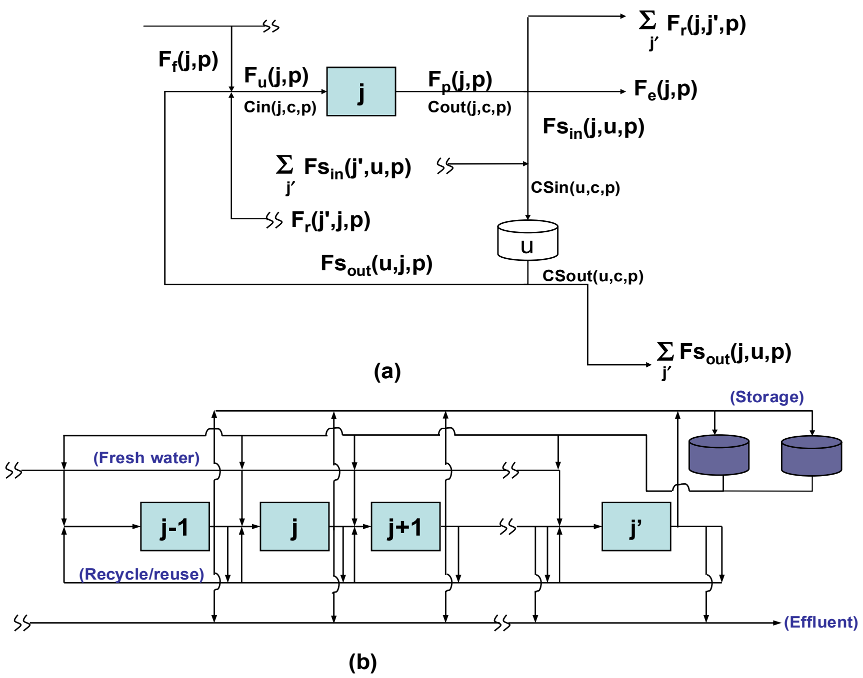


Figure 6. Superstructure for a water using unit (a) and the overall plant (b) for the distributed storage mathematical methodology

The mass balance constraints are the first constraints considered in the model as follows.

Mass balance constraints

The first constraints considered deal with the mass balances over a processing unit. As mentioned previously the water entering a processing unit is made up of wastewater that is directly recycled/reused, fresh water and wastewater from the various storage vessels. This is given in constraint (93). A similar constraint, constraint (94), is derived for the

outlet water from a unit. The water leaving a unit is either directly recycled/reused, sent to a storage vessel(s) or discarded as effluent.

$$F_u(j,p) = \sum_{j'} F_r(j',j,p) + F_f(j,p) + \sum_u Fs_{out}(u,j,p) \quad \forall\, j,j' \in J, p \in P, u \in U \qquad (93)$$

$$F_p(j,p) = \sum_{j'} F_r(j,j',p) + Fe(j,p) + \sum_u Fs_{in}(j,u,p) \quad \forall\, j,j' \in J, p \in P, u \in U \qquad (94)$$

Since the water contains contaminants, a contaminant balance has to be done on the inlet of the unit. The inlet concentration is thus defined by constraint (95). Here the contaminant mass into a unit is the sum of the contaminant mass from water that is directly recycled/reused and water from the various storage vessels. Important to note is that the balance is done for each contaminant present in the water.

$$C_{in}(j,c,p)F_u(j,p) = \sum_{j'} F_r(j',j,p)C_{out}(j',c,p) + \sum_u Fs_{out}(u,j,p)Cs_{out}(u,c,p) \\ \forall j,j' \in J, p \in P, c \in C, u \in U \qquad (95)$$

A contaminant mass balance over a unit has to be done as given in constraint (96). Here the mass of contaminants leaving a unit is the contaminant mass that has entered the unit and the mass load added to the water due to the operation in the processing unit. As with the inlet mass balance, this mass balance is done for each contaminant present in the system.

$$F_p(j,p)C_{out}(j,c,p) = F_u(j,p-1)C_{in}(j,c,p-1) + M_{lost}(c,j)y(s_{in},j,p-1), \\ \forall\, j \in J, p \in P, p > p_1, c \in C \qquad (96)$$

A product mass balance has to be done over the unit. The mass of raw material used is the sum of the mass of product produced and mass load given to the water. This is given in constraint (97).

$$m_u(s_{in}, j, p) = m_p(s_{out}, j, p) + \left(\sum_c M_{lost}(j,c)\right) y(s_{in}, j, p), \quad \forall s_{in} j \in J, p \in P, p > p_1, c \in C \tag{97}$$

There is a maximum allowable amount of water that each processing unit can use. Provided the amount of water used in the operation is below the physical limits of the vessel, the maximum amount of water is determined through concentration considerations. As with the multiple contaminant case, a limiting component can be defined. The limiting component is that component which requires the most amount of water to remain within the concentration limits for a given mass load. The maximum water used by a vessel is thus defined in constraint (98). The constraint states that the maximum amount of water is determined by the maximum ratio of a contaminant mass load and the difference between the maximum inlet and outlet concentrations.

$$\overline{F}_w(j) = max\left[\frac{M_{lost}(j,c)}{\overline{C}_{out}(j,c) - \overline{C}_{in}(j,c)}\right], \forall\ j \in J, c \in C \tag{98}$$

Since there is a maximum amount of water, water flows into a unit have to be constrained to that maximum. Constraint (99) ensures that the total amount of water going into a unit is less that the maximum, similar constraints are derived for water recycled/reused, given in constraint (100), and water reused from the various storage vessels, given in constraint (101).

$$F_u(j,p) \le \overline{F}_w(j) y(s_{in}, j, p) \quad \forall s_{in} \in S_{in}, j \in J, p \in P \tag{99}$$

$$F_r(j', j, p) \le \overline{F}_w(j) y_r(j', j, p) \quad \forall j', j \in J, p \in P \tag{100}$$

$$Fs_{out}(u, j, p) \le \overline{F}_w(j) ys_{out}(u, j, p) \quad \forall j \in J, p \in P, u \in U \tag{101}$$

The inlet concentration to a unit of each component present in the water also has to be constrained to a maximum, given in constraint (102). As does the outlet concentration of the water leaving a unit, given in constraint (103).

$$C_{in}(j,c,p) \le \overline{C}_{in}(j,c) y(s_{in}, j, p) \quad \forall s_{in} \in S_{in}, j \in J, p \in P, c \in C \tag{102}$$

$$C_{out}(j,c,p) \le \overline{C}_{out}(j,c) y(s_{in}, j, p-1) \quad \forall s_{in} \in S_{in}, j \in J, p \in P, p > p_1, c \in C \tag{103}$$

Mass balance constraints around each storage vessel also have to be defined. The first of these is a balance on the amount of water stored at a time point in each storage vessel, given in constraint (104). The amount of water stored at a time point in a particular storage vessel is the amount of water previously in the storage vessel and the difference between the inlet and outlet mass of water. This constraint for the first time point is defined in constraint (105), where the amount of water at the first time point is the difference between the amount of water initially in the storage vessel and the amount of water that is used from a storage vessel at the first time point.

$$qs(u,p) = qs(u,p-1) + \sum_j Fs_{in}(j,u,p) - \sum_j Fs_{out}(u,j,p), \quad \forall j \in J, p \in P, p > p_1, u \in U \tag{104}$$

$$qs(u,p) = Q_0 - \sum_j Fs_{out}(u,j,p), \forall\ j \in J, p \in P, p = p_1, u \in U \tag{105}$$

The inlet concentration into a storage vessel is defined in constraint (106), where the inlet constraint is the ratio of the contaminant mass of a particular contaminant and the amount of water going into a storage vessel. To ensure that the correct contaminants are stored in a particular storage vessel, the inlet concentration going into the storage vessel is constrained to a maximum, given in constraint (107). By setting the maximum concentration into a storage vessel to zero, one can control whether a certain contaminant can be stored in a particular vessel. The contaminant mass balance over a particular storage vessel is given in constraint (108). The constraint states that the amount of contaminant mass within a storage vessel is the amount stored in the previous time point and the difference between the amount leaving the vessel and entering the vessel. In the derivation of this constraint it is assumed that the storage vessel is ideally mixed, and hence the outlet concentration is the same as the concentration within the storage vessel. The concentration within the storage vessel at the first time point is defined in constraint (109).

$$CS_{in}(u,c,p) = \frac{\sum_j \left(Fs_{in}(j,u,p) C_{out}(j,c,p)\right)}{\sum_j Fs_{in}(j,u,p)}, \quad \forall\ j, j' \in J, p \in P, c \in C, u \in U \tag{106}$$

$$Cs_{in}(u,c,p) \leq \overline{C}s_{in}(u,c) \quad \forall\ p \in P, c \in C, u \in U \tag{107}$$

$$Cs_{out}(u,c,p)qs(u,p) = Cs_{out}(u,c,p-1)qs(u,p-1) + \sum_j Fs_{in}(j,u,p)Cs_{in}(u,c,p)$$
$$-\sum_j Fs_{out}(u,j,p)Cs_{out}(u,c,p), \quad (108)$$
$$\forall\ j \in J, p \in P, p > p_1, c \in C, u \in U$$

$$Cs_{out}(u,c,p) = Cs_{out}^{O}(u,c) \quad \forall u \in U, c \in C, p \in P, p = p_1 \quad (109)$$

The amount of water stored at a time point in a storage vessel has to be within the physical capacity of the storage vessel. This is ensured through constraint (110). Furthermore, the amount of water entering a storage vessel also has to be less than the capacity of the storage vessel, given in constraint (111). At the end of the time horizon one must also ensure that there is no water stored in each storage vessel. Constraint (112) ensures this.

$$qs(u,p) = Q^{\max}(u) \quad \forall\ p \in P, u \in U \quad (110)$$

$$Fs_{in}(j,u,p) \leq Q^{\max}(u) ys_{in}(j,u,p) \quad \forall\ j \in J, p \in P, u \in U \quad (111)$$

$$qs(u,p) = 0 \quad \forall\ p \in |P|, u \in U \quad (112)$$

In the constraints mentioned above there are various non-linear terms stemming from concentrations not being at their maximums. The non-linear terms take the form of bilinear terms, for which Quesada and Grossman (1995) proposed a linearization technique. During the application of the model to various examples it was noted that in practice only one term needed linearization. Linearization of other terms leads to excessive solution times. The linearization is explained below.

Let :

$$C_{out}(j,c,p)F_p(j,p) = \Gamma_1(j,c,p),$$

with the following bounds on each variable:

$$\begin{aligned} 0 \leq C_{out}(j,c,p) \leq \overline{C}_{out}(j,c) \\ 0 \leq F_p(j,p) \leq \overline{F}_w(j) \end{aligned},$$

then the following constraints hold.

$$\Gamma_1(j,c,p) \geq 0, \forall j \in J, p \in P, c \in C \tag{113}$$

$$\Gamma_1(j,c,p) \geq \overline{F}_w(j)C_{out}(j,c,p) + \overline{C}_{out}(j,c)F_p(j,p) - \overline{F}_w(j)\overline{C}_{out}(j,c)),$$
$$\forall j \in J, p \in P, c \in C \tag{114}$$

$$\Gamma_1(j,c,p) \leq \overline{F}_w(j)C_{out}(j,c,p), \quad \forall\, j \in J, p \in P, c \in C \tag{115}$$

$$\Gamma_1(j,c,p) \leq F_p(j,p)\overline{C}_{out}(j,c), \quad \forall\, j \in J, p \in P, c \in C \tag{116}$$

Substituting the linearised form of the bilinear term yields constraint (117), which is the partially linearised form of constraint (96).

$$\Gamma_1(j,c,p) = C_{in}(j,c,p-1)F_u(j,p-1) + M(j,c)y(j,p-1),$$
$$\forall j \in J, c \in C, p \in P, p > p_1 \tag{117}$$

The constraints above complete the mass balances constraints. Following these, constraints have to be developed to capture the essence of time.

Task Scheduling

The first constraints that are considered in scheduling are task scheduling constraints. The first of these is a duration constraint, given in constraint (118). The constraint states that the time at which a product is produced from a processing unit is the starting time and the duration of the operation.

$$t_p(j,p) = t_u(j,p-1) + \tau(j).y(j,p-1),$$
$$\forall j \in J, p \in P, p > p_1 \tag{118}$$

Constraint (119) states that a unit can only start operating once the unit has finished with a previous task. Constraint (120) ensures that raw material used at a later time point occurs at a later time. Constraint (121) is similar to the previous constraint, in that it applies to the time at which product is produced.

$$t_u(s_{in,}j,p) \geq t_p(s_{out},j,p) - H\left(2 - y(s_{in},j,p) - y(s_{in}',j,p-1)\right),$$
$$\forall\, j \in J, s_{in}, s_{in}' \in S_{in}, s_{out} \in S_{out}, p \in P, p > p_1 \tag{119}$$

$$t_u(s_{in}, j, p) \geq t_u(s_{in}', j, p') - H\left(2 - y(s_{in}, j, p) - y(s_{in}', j, p')\right),$$
$$\forall\, j \in J, s_{in}, s_{in}' \in S_{in}, p, p' \in P, p \geq p' \tag{120}$$

$$t_p(s_{out}, p) \geq t_p(s_{out}', j, p') - H\left(2 - y(s_{in}, j, p-1) - y(s_{in}', j, p'-1)\right),$$
$$\forall\, j \in J, s_{in}, s_{in}' \in S_{in}, s_{out} s_{out}' \in S_{out}, p, p' \in P, p \geq p' \tag{121}$$

Recycle scheduling

Constraint (122) states that if there is recycle/reuse taking place the unit receiving the water must be operating at that time point. However, recycling/reusing of water is not a prerequisite for a unit to operate. The binary variable is summed over all the states to ensure that the recycle of water is state independent. There will only ever be one operation happening in a unit at a certain time point, hence the summation will never take on a value larger than one. To ensure that this is the case constraint (123) is defined.

$$y_r(j, j', p) \leq \sum_{s_{in}} y(s_{in}, j', p), \ \forall\, s_{in} \in S_{in}, p \in P, j, j' \in J \tag{122}$$

$$\sum_{s_{in}} y(s_{in}, j, p) \leq 1, \ \forall\, s_{in} \in S_{in}, p \in P, j \in J \tag{123}$$

The following two constraints are derived to ensure that the time at which water is recycled/reuse coincides with the time at which the water was produced, given in constraints (124) and (125).

$$t_r(j, j', p) \leq t_p(s_{out}, j, p) + H\left(2 - y_r(j, j', p) - y(s_{in}, j, p-1)\right),$$
$$\forall\, j, j' \in J, s_{in} \in S_{in}, s_{out} \in S_{out}, p \in P, p > p_1 \tag{124}$$

$$t_r(j, j', p) \geq t_p(s_{out}, j, p) - H\left(2 - y_r(j, j', p) - y(s_{in}, j, p-1)\right),$$
$$\forall\, j, j' \in J, s_{in} \in S_{in}, s_{out} \in S_{out}, p \in P, p > p_1 \tag{125}$$

Similar constraints hold to ensure that the time at which water is recycled/reused to a unit coincides with the time at which the unit begins to operate, stated in constraints (126) and (127).

$$t_r(j,j',p) \le t_u(s_{in},j',p) + H\left(2 - y_r(j,j',p) - y(s_{in},j',p)\right),\quad \forall\, j,j' \in J, s_{in} \in S_{in}, p \in P \tag{126}$$

$$t_r(j,j',p) \ge t_u(s_{in},j',p) - H\left(2 - y_r(j,j',p) - y(s_{in},j',p)\right),\quad \forall\, j,j' \in J, s_{in} \in S_{in}, p \in P \tag{127}$$

Following direct recycle/reuse of water, scheduling constraints have to be formulated for the indirect reuse of water through the various storage vessels.

Storage Scheduling

The first constraints considered in this section ensure that the time at which water is transferred to a storage vessel coincides with the time at which that water is produced, given in constraints (128) and (129). Constraint (130) states that if water is being transferred to a storage vessel then the unit from which the water came must have operated in the previous time point. However, a unit does not necessarily have to send water to a specific tank each time it operates.

$$ts_{in}(j,u,p) \ge t_p(s_{out},j,p) - H\left(2 - ys_{in}(j,u,p) - y(s_{in},j,p-1)\right),\quad \forall\, j \in J, s_{in} \in S_{in}, s_{out} \in S_{out}, p \in P, p > p_1, u \in U \tag{128}$$

$$ts_{in}(j,u,p) \le t_p(s_{out},j,p) + H\left(2 - ys_{in}(j,u,p) - y(s_{in},j,p-1)\right),\quad \forall\, j \in J, s_{in} \in S_{in}, s_{out} \in S_{out}, p \in P, p > p_1, u \in U \tag{129}$$

$$ys_{in}(j,u,p) \le \sum_{s_{in}} y(s_{in},j,p-1),\quad \forall\, s_{in} \in S_{in}, j \in J, p \in P, p > p_1, u \in U \tag{130}$$

Similar constraints hold for the water leaving a storage vessel, where the time at which water is sent to a storage vessel must coincide with the time at which a unit starts operating. This is given in constraints (131) and (132). Furthermore, if water is going from a storage vessel to a unit, the unit receiving the water must operate at that time point. However, it is not a prerequisite for a unit to receive water from a storage vessel when it operates. This is given in constraint (133).

$$ts_{out}(u,j,p) \geq t_u(s_{in},j,p) - H\left(2 - ys_{out}(j,p) - y(s_{in},j,p)\right),$$
$$\forall\ j \in J, s_{in} \in S_{in}, u \in U, p \in P \tag{131}$$

$$ts_{out}(u,j,p) \leq t_u(s_{in},j,p) + H\left(2 - ys_{out}(u,j,p) - y(s_{in},j,p)\right),$$
$$\forall\ j \in J, s_{in} \in S_{in}, u \in U, p \in P \tag{132}$$

$$ys_{out}(u,j,p) \leq \sum_{s_{in}} y(s_{in},j,p), \forall\ s_{in} \in S_{in}, j \in J, p \in P \tag{133}$$

Further scheduling constraints have to be derived to ensure the correct scheduling of the streams entering and leaving a storage vessel. Constraint (134) ensures that water leaving a storage vessel at a later time point coincides with a later time. Constraints (135) and (136) ensure that the time at which water leaves a storage vessel to various units at a time point occur at the same time.

$$ts_{out}(u,j,p) > ts_{out}(u,j',p') - H\left(2 - ys_{out}(u,j,p) - ys_{out}(u,j',p')\right),$$
$$\forall\ j,j' \in J, u \in U, p,p' \in P, p > p' \tag{134}$$

$$ts_{out}(u,j,p) \geq ts_{out}(u,j',p) - H\left(2 - ys_{out}(u,j,p) - ys_{out}(u,j',p)\right),$$
$$\forall\ j,j' \in J, u \in U, p \in P \tag{135}$$

$$ts_{out}(u,j,p) \leq ts_{out}(u,j',p) + H\left(2 - ys_{out}(u,j,p) - ys_{out}(u,j',p)\right),$$
$$\forall\ j,j' \in J, u \in U, p \in P \tag{136}$$

Similar constraints hold for water entering a storage vessel. Namely, water entering a storage vessel at a later time point must occur at a later time, given in constraint (137). Water entering a storage vessel from various sources at a time point must occur at the same time, constraints (138) and (139).

$$ts_{in}(j,u,p) > ts_{in}(j',u,p') - H\left(2 - ys_{in}(j,u,p) - ys_{in}(j',u,p')\right), \quad \forall\ j,j' \in J, u \in U, p,p' \in P, p > p' \tag{137}$$

$$ts_{in}(j,u,p) \geq ts_{in}(j',u,p) - H\left(2 - ys_{in}(j,u,p) - ys_{in}(j',u,p)\right), \quad \forall\ j,j' \in J, u \in U, p \in P \tag{138}$$

$$ts_{in}(j,u,p) \leq ts_{in}(j',u,p) + H\left(2 - ys_{in}(j,u,p) - ys_{in}(j',u,p)\right), \quad \forall\ j,j' \in J, u \in U, p \in P \tag{139}$$

Water leaving a storage vessel at a later time point must happen at a later time than the time at which water entered the storage vessel at the earlier time point, given in constraint (140). If water is entering and leaving a storage vessel at a time point, then this must occur at the same time, given in constraints (141) and (142).

$$ts_{out}(u,j,p) > ts_{in}(j',u,p') - H\left(2 - ys_{out}(u,j,p) - ys_{in}(j',u,p')\right), \quad \forall\ j,j' \in J, u \in U, p,p' \in P, p > p' \tag{140}$$

$$ts_{out}(u,j,p) \geq ts_{in}(j',u,p) - H\left(2 - ys_{out}(u,j,p) - ys_{in}(j',u,p)\right), \quad \forall\ j,j' \in J, u \in U, p \in P \tag{141}$$

$$ts_{out}(u,j,p) \leq ts_{in}(j',u,p) + H\left(2 - ys_{out}(u,j,p) - ys_{in}(j',u,p)\right), \quad \forall\ j,j' \in J, u \in U, p \in P \tag{142}$$

It is important to note that the above constraints hold for every storage vessel in the system and that each storage vessel is dealt with independently.

Time horizon constraints

The final constraints necessary to complete the scheduling model are constraints that ensure that all operations occur within the time horizon, given in constraints (143)-(147).

$$ts_{in}(j,u,p) \le H, \quad \forall\, j \in J, u \in U, p \in P \tag{143}$$

$$ts_{out}(u,j,p) \le H, \quad \forall\, j \in J, u \in U, p \in P \tag{144}$$

$$t_u(j,p) \le H, \quad \forall\, j \in J, p \in P \tag{145}$$

$$t_p(j,p) \le H, \quad \forall\, j \in J, p \in P \tag{146}$$

$$t_r(j,j',p) \le H, \quad \forall\, j, j' \in J, p \in P \tag{147}$$

Objective function

The objective function used in the model is the maximisation of revenue, where the revenue is given in Equation (148). The revenue is the difference between the profit due to the production of product, the cost of raw materials and the treatment costs of the effluent water.

$$max\ R = \sum_p \left(\sum_{s_{in}, s_{out}, j} SP(s_{out}) m_p(s_{out}, j, p) - \sum_j CR(s_{in}) m_u(s_{in}, j, p) - CE \sum_j F_e(j,p) \right) \tag{148}$$

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

4. PRACTICAL IMPLEMENTATION OF THE DEVELOPED METHODOLOGY

As mentioned in Chapter 1 of this report, the industrial site of choice for practical implementation of the developed methodology, was a pharmaceutical production facility. Its features fully dovetailed with the project objectives (see Section 1.1.3).

4.1 Industrial Test Site Background

The pharmaceutical operation produces mainly liquid products and women's sanitary products. The plant operates mainly in batch mode when producing the liquid products. This is due to the need to produce a wide variety of products in small amounts. Water usage on site averages about 90 000 m^3 per annum. Wastewater is discarded to a small treatment plant on site. The water from the treatment plant is then fed into the municipal system for further treatment.

The plant can roughly be divided into three main sections, namely the pharmaceutical mixing area, the toiletries mixing area and the women's sanitary product area. As the water usage was highest in the pharmaceutical and toiletries area, these areas became the main focus of water minimisation.

Water in the pharmaceuticals area is mainly used in product formulation, cleaning and temperature control. This is very similar in the toiletries area. The pharmaceutical area has six mixers within the area, three of which are dedicated to a small range of water based products, another two are dedicated to a different set of oil based products and the last remaining mixer produces a wide variety of products, such as creams and lotions.

The toiletries area consists of five mixers, one is dedicated to oil based products and the other four could produce a wide range of products (creams, lotions, deodorants and shampoos). Apart from the mixing vessels in the area there are also intermediate product storage vessels. The storage tanks are either in the form of platecons (square containers with a removable plastic inner bag for product) or fixed storage vessels.

In addition to the mixing and storage vessels there are also packaging lines. Due to the relatively small amount of water that is used by the packaging lines they were not focused on in this study. The breakdown of the water usage at the industrial site is given in Figure 7.

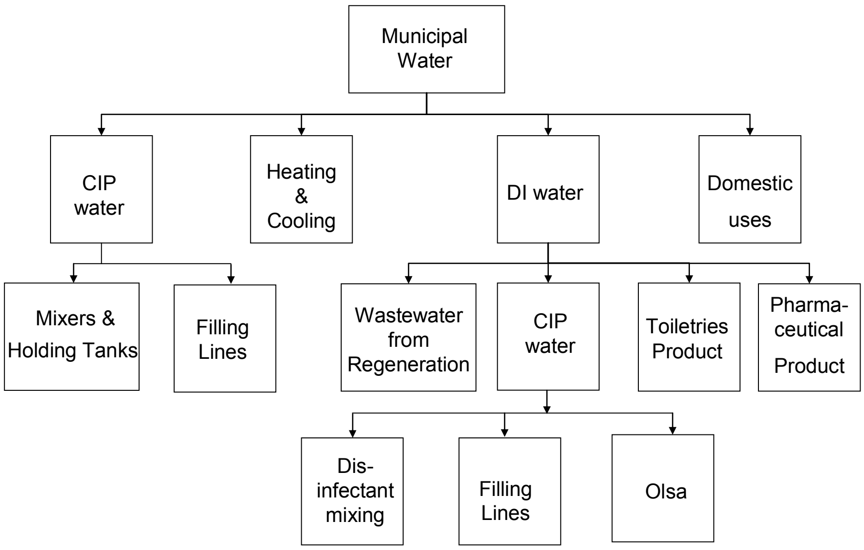


Figure 7. Breakdown of the water usage at the industrial site

Wastewater minimisation at the industrial site is broken up into two sections. The first section deals with the application of the derived wastewater minimisation methodology to the plant. The application of the methodology was done in three steps, with the final step involving the application of a final methodology specifically tailored to the operation at the industrial site. The second section deals with wastewater minimisation through process related changes. The changes are included as they provide substantial savings in the water used on the plant and the capital costs of the changes are relatively little.

4.2 Application of Mathematical Methodology to the Industrial site

Currently the industrial site has no formal scheduling methodology or water saving strategy. Upon assessment of the plant, the area where scheduling together with wastewater minimisation could take place was the toiletries mixing area. Here water is used for washing out of vessels. Observations on the concentration of contaminants within the washout water showed that there were certain steps within the washout procedure that had relatively low concentrations. This facilitated the reuse of the water within another washout cycle.

The products produced in the area were grouped into four groups of products, namely, lotions, creams, shampoos and deodorants. Mixing times of the various products were available through in-house standards. The required production of each product for a certain time horizon was known, thus the main aim of the scheduling problem was to determine which mixers would produce which products, while taking possible reuse of water for washouts into consideration.

The washout of a mixing vessel, currently, can be seen as a continuous process that takes place for a certain time in the mixer. Water is constantly discarded down the drain while fresh water is added. In the application of the methodology it is, however, assumed that the washout is a completely batch process, i.e. water is used at the beginning of the washout and then produced at the end of a washout. This type of operation can be achieved with the current mixers, with the addition of a direct recycle line.

The application of the mathematical methodology was done in three steps. The first step was a preliminary application of the methodology derived by Majozi (2005a) to the mixing area to identify data that was needed and practical considerations that needed to be taken into account. This also gave an idea of the general size of the resulting model and assumptions that would be needed to ensure solutions are found. During the first phase, the scheduling of fixed storage vessels was taken into consideration in conjunction with the mixing vessels. The second stage took some practical considerations into account, more specifically the compatibility of washout water and product residue. The final step was the development of a model that could be applied in practice. During the year an important change was made to the washout procedure of the mixing and storage vessels, namely the move from chemical sanitising to heat sanitising. This gave the opportunity to practically reuse water and derive a model accordingly, thus the final model was derived.

4.2.1 First investigation

As a preliminary study into the operation at the industrial site the process was modelled in a simplified manner, as a single contaminant system. This gave insight into any practical considerations and possible inaccuracies with data used.

The operation at the industrial site has special features that had to be included for a reasonably accurate representation of the process. The first is that the wastewater produced at the industrial site is from washouts only. The production of product does not directly produce any water by-products. This is a change from the operations that were envisaged by Majozi (2005a) during the derivation of the model. In the application of the wastewater minimisation methodology it is assumed that a washout will always happen after a product has been removed from a mixer. This is a reasonable assumption as this was most often the case in the mixing area.

The resulting model was solved for various scenarios and the following was concluded from the investigation:

- Compatibility of wastewater and product residue needed to be taken into account
- Corporate requirements for reuse of water needed to be checked
- Preferential mixing of certain products in certain mixers needed to be addressed
- Consideration of different washout steps might need addressing
- Different sized mixers need to be taken into account
- More accurate outlet concentrations are needed and,
- Water amounts for washouts should be investigated

Furthermore, the model drastically increased in size, with long solution times, when the product storage vessels were taken into consideration. The time at which a storage vessel is washed is also determined by the time at which product is removed from the vessel. The time at which product is removed is determined by the packaging lines. Hence proper scheduling of washouts of the storage vessels was virtually impossible since the washout times were determined by the product packaging lines which did not form part of the model. Therefore product storage vessels were ignored.

From the above results, a second model that could take product compatibilities into consideration was used. For the second case the derived multiple contaminant model (Majozi and Gouws, 2007), presented earlier in section 3.1, was applied to the mixing area.

4.2.2. Secondary study

Compatibility between wastewater and product residue has to be taken into account when one is considering reuse of washout water containing product. There are several reasons for this. Reuse of washout water must ensure that the washout with the reused water is just as effective as with fresh water. Wastewater with certain residues is not suitable for reuse because they could leave small amounts of the residue, present in the wastewater, in the vessel after a washout. This is specifically the case with wastewater containing deodorant residue. The deodorant is by nature hydrophobic and will not dissolve readily in water. If washout water containing deodorant residue is reused it is very possible that a small amount of deodorant will remain in the mixer being washed after the washout due to undissolved deodorant. The next main reason is that certain products might force each other out of solution, hence causing unwanted residues in the mixer.

Product residue and contaminant compatibilities can only effectively be dealt with by seeing the problem as a multiple contaminant problem. The methodology by Majozi (2005a) was extended by Majozi and Gouws (2007) to include multiple contaminants and was applied to the operation at the industrial site.

In this study more accurate data was used for the outlet concentrations and the estimated amount of water used for the washout in complete batch mode was possibly closer to true amounts. Preferential mixing of products in mixers was ensured by assuming that each mixer was dedicated to the mixing of a certain product.

An example of the typical scheduling problem for the second case study is presented below. The example involves the scheduling of the four mixers within the toiletries area. For the secondary study it is assumed that each mixer produces a certain product. Mixer one produces only shampoo's, mixer 2 produces only deodorants, mixer 3 produces only lotions and mixer 4 produces creams only. The multiple contaminant model presented above was tailored to the operation at the industrial site.

For each mixer the maximum allowable inlet concentration of the water used for a washout is given in Table 1. The maximum inlet concentrations are not necessarily accurate, but for the purpose of the investigation proved to be sufficient. Important to note from the maximum inlet concentrations is that wastewater reused in mixers 1, 3 and 4 cannot contain any deodorant. The corresponding maximum inlet concentration of the deodorant in these mixers is zero.

Table 1. Maximum inlet concentrations used for example

	Shampoo (kg prod. /kg water)	**Deodor. (kg prod. /kg water)**	**Lotion (kg prod. /kg water)**	**Creams (kg prod. /kg water)**
Mixer 1	0.014	0	0.007	0.0035
Mixer 2	0.014	0.0035	0.007	0.007
Mixer 3	0.014	0	0.007	0.0035
Mixer 4	0.014	0	0.007	0.0035

Further data required for the solution of the example is given in Table 2. The durations given in Table 2 are the industrial standards used on the plant. The residue mass and maximum outlet concentrations were estimated from observations on the plant. The maximum water used for each mixer was determined using constraint (10). Important to note is that since there is only one type of residue left in each mixer, only the corresponding concentration of that residue in the wastewater will change.

Table 2. Data for secondary study illustrative example

Mixer Number	**Duration (h)**	**Residue (kg)**	**Maximum water (kg)**	**Maximum outlet conc. (kg prod. /kg water)**
1 (Shampoos)	7	15	576.9	0.04
2 (Deodorants)	5.5	15	361.4	0.045
3 (Lotions)	11	30	1238.9	0.05
4 (Creams)	11	70	697.6	0.06

A typical number of batches of each product over 24 hours are given in Table 3.

Table 3. Number of batches to be produced

Product	**Number of Batches**
Shampoo	2
Deodorant	3
Cream	1
Lotion	2

The resulting schedule is given in Figure 8. The black numbers in the figure represent the amount of fresh water used for the washout. The bold black numbers represent the amount of water that is used from the storage vessel, the amount of water that was reused directly and the amount of water that was sent to storage. All water amounts are in kilograms. In the figure, unit 1 sends its water to the storage tank at time 7.5hr and at 15hr, it also receives some of its water from the storage vessel at 14.5hr. Unit 2 receives water from the storage vessel at 17.5hr and receives water from unit 3 via direct reuse at time 23.5hr. Unit 3 receives an additional amount of water from the storage tank for its washout. Unit 4 does not receive any water from either the storage vessel or via direct reuse from another unit.

The problem was solved in GAMS using the DICOPT algorithm. The NLP solver was CONOPT and the MIP solver was CPLEX. The solution took 106.5 CPU seconds and had 364 binary variables. The optimum number of time points was 13. The total amount of effluent produced is 3 325.1 kg, which is 19.2% lower than the operation without recycle/reuse of the wastewater.

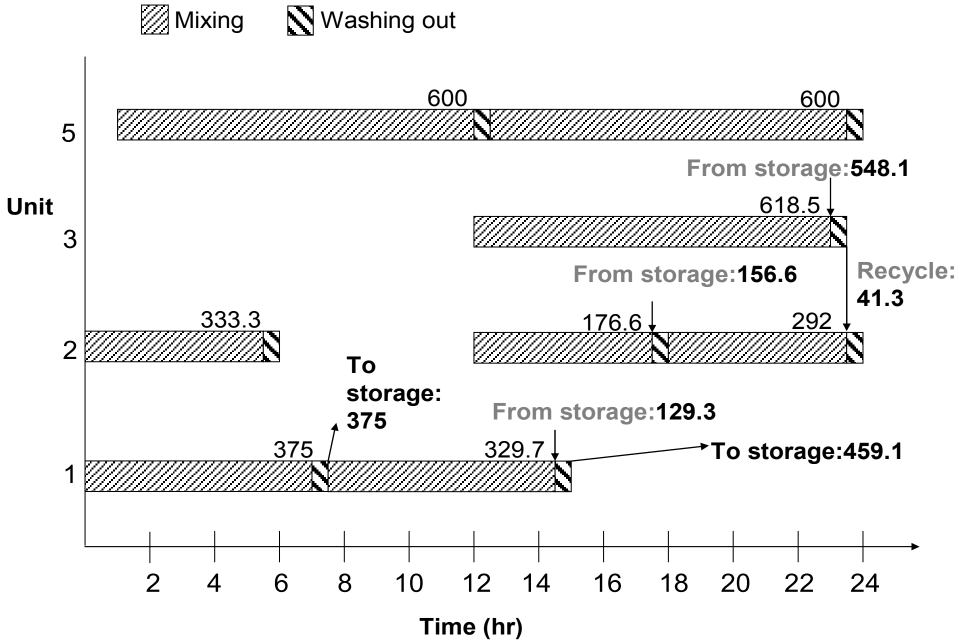


Figure 8. Production schedule produced from secondary study

Important to note is that none of the water produced by unit 2 is reused in other units. This is in line with the inlet concentration requirements of the other units. However, a further savings in the amount of water might have been achieved had there been a dedicated storage vessel for the reuse of wastewater from mixer 2.

The multiple contaminant model applied to the mixing area was not necessarily practically implementable. This was due to the need for changes in the method of washout, i.e. changing from a continuous type washout to a batch type washout, and concerns over the general lack of data on the reuse of washout water. However, due to the change from chemical sanitising to heat sanitising the opportunity arose to derive a model based on this with practical applicability. Due to the change in sanitising method, the sanitising water was reusable. The final model derived takes this into account.

4.2.3 Final model

The water considered for reuse in the final model was the water used for the sanitising step of the washout. This water lends itself to reuse as the water contains low levels of contaminants and is sanitary due to the elevated temperature of the water. There is an intermediate storage tank available for the water (the cleaning in place(CIP) tank), hence there was no need to purchase any equipment to implement the methodology. The required piping was installed in a project described further on.

In the methodology the CIP tank was seen as the central storage vessel for the reuse of wastewater. Furthermore direct reuse of water was discarded as this is particularly difficult to implement practically. In this situation, water can only be reused through the CIP tank, i.e. no connections between mixing vessels can be made. Only the water entering the washout for the first step and the water produced at the end of the sanitising step was considered. This was done because water used for the chemical wash, second rinse and sanitising water (the sanitising water referred to here is at the beginning of the sanitising step) had no effect on the scheduling aspect of the problem. Water used for the chemical wash and second rinse is fresh water. This water goes continuously down the drain during the washout. At the beginning of the sanitising step CIP tank is filled and the sanitising step is thus fed by fresh water at the beginning. During the sanitising step and at the end of the sanitising step water is re-circulated to the CIP tank.

Reuse of water in the manner explained has certain implications on the scheduling methodology. This has mainly to do with the fact that the reuse of wastewater is not constrained by inlet or outlet concentrations, but rather availability of the water and the fact that only one washout can take place at a time.

Not having to take concentration into consideration means that all the constraints in the methodology that deal with concentrations could be done away with. This included contaminant mass balances and maximum inlet and outlet concentrations. Compatibility of wastewater is also no issue as there was no product in the sanitising water. A full description of the final model is given below

The final developed mathematical model

The following sets, variables and parameters were used in the model.

Sets

$P = \{p \mid p = \text{time point}\}$
$M = \{m \mid m = \text{mixer}\}$
$S_{in} = \{s_{in} \mid s_{in} = \text{input state into a unit, i.e. raw material}\}$
$S_{out} = \{s_{out} \mid s_{out} = \text{output state from a unit, i.e. product}\}$

Variables

$m_u(s_{in},m,p)$	mass of raw material used in mixer *m* at time point *p*
$m_p(s_{out},m,p)$	mass of product produced from mixer *m* at time point *p*
$f_f(m,p)$	mass of fresh water used for a washout in mixer *m* at time point *p*
$fe(m,p)$	mass of water as effluent after a washout from mixer *m* at time point *p*
$fs_{in}(m,p)$	mass of water sent to the CIP tank after a washout of mixer *m* at time point *p*
$fs_{out}(m,p)$	mass of water sent from the CIP tank to a mixer for a washout
$f_w(m,p)$	total mass of water used for a washout of mixer *m* at time point *p*
$t_u(s_{in},m,p)$	time at which a mix begins in mixer *m* at time point *p*
$t_p(s_{out},m,p)$	time at which product is produced from a mixer *m* at time point *p*
$t_{uw}(m,p)$	time at which a washout starts in mixer *m* at time point *p*
$t_{pw}(m,p)$	time at which a washout ends in mixer *m* at time point *p*
$ts_{in}(m,p)$	time at which water goes to the CIP tank from a mixer *m* at time point *p*
$ts_{out}(m,p)$	time at which water leaves the CIP tank to a mixer *m* at time point *p*
$y(s_{in},m,p)$	binary variable for usage of a mixer for a certain product at a certain time point
$y_w(m,p)$	binary variable for a washout
$ys_{in}(m,p)$	binary variable for the reuse of water to the CIP tank from a mixer
$ys_{out}(m,p)$	binary variable for the reuse of water from the CIP tank to a mixer

Parameters

$M_{res}(m)$	residue mass after a product has been removed from a mixer
$M_u(s_{in})$	mass of raw material used for a product
$F(m)$	amount of water used for a washout
Q_s^o	initial amount of water in the CIP tank
$\overline{Q}$	maximum amount of water that can be stored in the CIP tank
$\tau(s_{in},m)$	mixing duration of a certain product in a specific mixer
τ_{wash}	duration of a washout

The mathematical formulation is based on the superstructure given in Figure 9. The figure is representative of a mixer. The figure shows all the flows to and from the mixer.

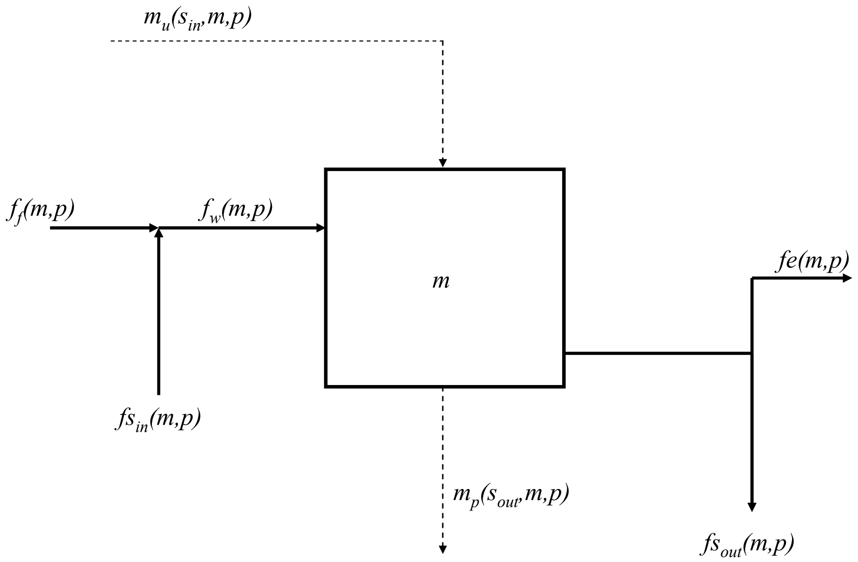


Figure 9. Superstructure showing a water using operation in the final mathematical model

Due to the nature of the operation at the industrial site, special attention needs to be paid to the number of time points used to describe each operation.

Time points

The number of time points used to describe the operation at the industrial site is different to a general type of operation. This is because two distinct operations take place within a mixer when product is produced. The mixer first mixes product, the product is removed and then the mixer is washed. This then means that three time points are necessary to fully describe a mixer's operation. At the first time point the mixer begins a mix. At the second time point the mixed product is removed and a washout begins. Finally at the third time point the washout ends. The impact of the number of time points is seen in some of the constraints that are used in the model.

The first step in the description of the mathematical model is the mass balance constraints.

Mass balance constraints

The first mass balance considered is the product mass balance. The amount of raw material into a mixer is a fixed amount. This is given in equation (149). The amount of mixed product produced is the difference between the amount of raw materials that entered the mixer and the amount of residue that is left in the mixer. This is given in constraint (150).

$$m_u(s_{in}, m, p) = M_u(s_{in})y(s_{in}, m, p), \forall\ s_{in} \in S_{in}, p \in P, m \in M \tag{149}$$

$$\begin{gathered} m_p(s_{out}, m, p) = m_u(s_{in}, m, p-1) - M_{res}(m)y(s_{in}, m, p-1), \\ \forall\ s_{in} \in S_{in}, p \in P, p > p_1, u \in U, m \in M \end{gathered} \tag{150}$$

After the product mass balances, one has to consider the mass balance over the washout water. The water considered in this methodology is only water used for the first washout and the sanitising water. The amount of water used for a washout is fixed. This is given in constraint (151). This is different to the original concentration based method where the amount of water used for a washout is free to vary. The water used for a washout can either be fresh water or water used from a previous sanitising step, this water is stored in the CIP tank. Constraint (152) captures this. Constraint (153) is an outlet water balance. The constraint states that water exiting a mixer from a washout can either be discarded as effluent or sent to the CIP tank for reuse. It is assumed that the whole amount of washout water is either reused or discarded as effluent, but not both. This means that the amount of water reused is equal to the total amount of water into a vessel for a washout. This is given in constraint (154). It is important to note that reuse of the washout water occurs solely through the CIP tank and that there is no opportunity to reuse the water directly from one mixer to another mixer.

$$f_w(m, p) = F_w(m)y_w(m, p-1)\ \forall\ p \in P, p > p_1, m \in M \tag{151}$$

$$f_w(m, p) = f_f(m, p) + fs_{out}(m, p)\ \forall\ m \in M, p \in P \tag{152}$$

$$f_w(m, p-1) = fe(m, p) + fs_{in}(m, p), \forall\ m \in M, p \in P, p > p_1 \tag{153}$$

$$fs_{in}(m, p) = F_w(m)ys_{in}(m, p), \forall\ p \in P, m \in M \tag{154}$$

Constraint (155) ensures that the amount of water used from the CIP tank does not exceed the amount of water used for a washout.

$$fs_{out}(m, p) \leq F_w(m)ys_{out}(m, p), \forall\ p \in P, m \in M \tag{155}$$

The final mass balances that need to be considered are the mass balances around the CIP tank. The amount of water in the CIP tank is the amount of water stored at the previous time point and the difference between the inlet and outlet amounts. This is given in constraint (156). At the beginning of the time horizon the amount of water stored at the first time point is the difference in the amount of water initially in the CIP tank and the amount of water used for a washout. This is given in constraint (157). Furthermore constraint (158) ensures that the amount of water in the CIP tank does not exceed the capacity of the tank.

$$q(p) = q(p-1) + \sum_m fs_{in}(m,p) - \sum_m fs_{out}(m,p),\ \forall\ m \in M, p \in P, p > p_1 \tag{156}$$

$$q(p_1) = Q_s^0 - \sum_m fs_{out}(m,p_1),\ \forall\ m \in M \tag{157}$$

$$q(p) \le \overline{Q}, \forall\ p \in P \tag{158}$$

Following the mass balances one has to consider sequencing and scheduling constraints to ensure that the essence of time is captured.

CIP storage tank sequencing and scheduling

Constraints (159) and (160) ensure that when water is transferred to the CIP tank the time coincides with the ending of a washout. Constraint (161) ensures that if water is transferred to the CIP tank the mixer did indeed have a washout beforehand. It is possible, however, that a washout occurs and no water is sent to the CIP tank.

$$ts_{in}(m,p) \ge t_{pw}(m,p) - H\left(1 - ys_{in}(m,p)\right), \forall\ m \in M, p \in P \tag{159}$$

$$ts_{in}(m,p) \le t_{pw}(m,p) + H\left(1 - ys_{in}(m,p)\right),\ \forall\ m \in M, p \in P \tag{160}$$

$$ys_{in}(m,p) \le y_w(m,p-1),\ \forall\ m \in M, p \in P, p > p_1 \tag{161}$$

Constraints (162) and (163) ensure that the time at which water is transferred to a mixer from the CIP tank coincides with the beginning of a washout. Constraint (164) is similar to constraint (138) in that water can only be transferred if there is a washout taking place at that time point.

$$ts_{out}(m,p) \ge t_{uw}(m,p) - H\left(1 - ys_{out}(m,p)\right), \forall\ m \in M, p \in P \tag{162}$$

$$ts_{out}(m,p) \le t_{uw}(m,p) - H\left(1 - ys_{out}(m,p)\right), \forall\ m \in M, p \in P \quad (163)$$

$$ys_{out}(m,p) \le y_{w}(m,p),\ \forall\ m \in M, p \in P \quad (164)$$

Constraint (165) ensures that water transferred from the CIP tank to a mixer at a later time point corresponds to a later time. Constraints (166) and (167) ensure the time at which water is transferred from the CIP tank to different mixers at the same time point corresponds to the same time.

$$ts_{out}(m,p) \ge ts_{out}(m',p') - H\left(2 - ys_{out}(m,p) - ys_{out}(m',p')\right), \forall\ m,m' \in M, p,p' \in P, p' < p \quad (165)$$

$$ts_{out}(m,p) \ge ts_{out}(m',p) - H\left(2 - ys_{out}(m,p) - ys_{out}(m',p)\right), \forall\ m,m' \in M, p \in P \quad (166)$$

$$ts_{out}(m,p) \le ts_{out}(m',p) + H\left(2 - ys_{out}(m,p) - ys_{out}(m',p)\right), \forall\ m,m' \in M, p \in P \quad (167)$$

Constraint (168) ensures that water transferred to the CIP tank at a later time point corresponds to a later time. Constraints (169) and (170) ensure that the time at which multiple water streams enter the CIP tank at a time point is the same.

$$ts_{in}(m,p) > ts_{in}(m',p') - H\left(2 - ys_{in}(m,p) - ys_{in}(m',p')\right), \forall\ m,m' \in M, p,p' \in P, p > p' \quad (168)$$

$$ts_{in}(m,p) \ge ts_{in}(m',p) - H\left(2 - ys_{in}(m,p) - ys_{in}(m',p)\right), \forall\ m,m' \in M, p \in P \quad (169)$$

$$ts_{in}(m,p) \le ts_{in}(m',p) + H\left(2 - ys_{in}(m,p) - ys_{in}(m',p)\right), \forall\ m,m' \in J, p \in P \quad (170)$$

Constraint (171) ensures that water transferred to a mixer a later time point happens at a later time than water transferred to the CIP at an earlier time point. Constraints (172) and (173) ensure that the time at which water enters and leaves the CIP tank at a time point happens at the same time.

$$ts_{out}(m,p) > ts_{in}(m',p') - H\left(2 - ys_{out}(m,p) - ys_{in}(m',p')\right), \forall\ m,m' \in M, p,p' \in P, p > p' \quad (171)$$

$$ts_{out}(m,p) \geq ts_{in}(m',p) - H\left(2 - ys_{out}(m,p) - ys_{in}(m',p)\right), \forall\ m,m' \in M, p \in P \tag{172}$$

$$ts_{out}(m,p) \leq ts_{in}(m',p) + H\left(2 - ys_{out}(m,p) - ys_{in}(m',p)\right), \forall\ m,m' \in M, p \in P \tag{173}$$

Since there is at most only one mixer transferring water to the CIP tank at a time point constraints (169) and (170) become redundant. This is similar to constraints (166) and (167), where at there will only be one water stream leaving the CIP tank at any given time. The reason for the above is because there will only ever be one washout happening at a time.

Washout scheduling

It is assumed in the model that the washout of a mixer occurs directly after the product has been pumped out of the mixer. Constraints (174) and (175) ensure that the washout starts at the time at which the product is fully removed.

$$t_p(s_{out},m,p) \geq t_{uw}(m,p) - H\left(2 - y(s_{in},m,p-1) - y_w(m,p)\right),$$
$$\forall\ m \in M, p \in P, p \geq p_1, s_{in} \in S_{in} \tag{174}$$

$$t_p(s_{out},m,p) \leq t_{uw}(m,p) - H\left(2 - y(s_{in},m,p-1) - y_w(m,p)\right),$$
$$\forall\ m \in M, p, p' \in P, p \geq p_1, s_{in} \in S_{in} \tag{175}$$

Horizon constraints

Constraints (176)-(181) ensure that all operations and times are within the specified time horizon.

$$ts_{in}(m,p) \leq H, \quad \forall m \in M, p \in P \tag{176}$$

$$ts_{out}(m,p) \leq H, \quad \forall m \in M, p \in P \tag{177}$$

$$t_u(s_{in},m,p) \leq H, \quad \forall m \in M, p \in P, s_{in} \in S_{in} \tag{178}$$

$$t_p(s_{out},m,p) \leq H, \quad \forall m \in M, p \in P, s_{out} \in S_{out} \tag{179}$$

$$t_{uw}(m,p) \leq H, \quad \forall m \in M, p \in P \tag{180}$$

$$t_{pw}(m,p) \leq H, \quad \forall m \in M, p \in P \tag{181}$$

Duration constraints

Constraint (182) defines the beginning and ending times of a mix. Here the ending time is the time at which the mix starts and the duration of the mix in the mixer. This is similar for the washout, given in constraint (183).

$$t_p(s_{out}, m, p) = t_u(s_{in}, m, p-1) + \tau(s_{in}, m)y(s_{in}, m, p-1) \quad \forall\, m \in M, p \in P, p > p_1, s_{in} \in S_{in}, s_{out} \in S_{out} \tag{182}$$

$$t_{pw}(m, p) = t_{uw}(m, p-1) + \tau_{wash}(m)y_w(m, p-1) \; \forall\, m \in M, p \in P, p > p_1 \tag{183}$$

Mixer scheduling

Constraint (184) ensures that the time at which a mixer starts a mix is after the washout has finished.

$$t_u(s_{in}, m, p) \geq t_{pw}(m, p) - H\left(1 - y(s_{in}, m, p-1)\right) \quad \forall\, m \in M, p \in P, p \geq p_1, s_{in} \in S_{in} \tag{184}$$

Constraint (185) ensures that the starting time of each mix corresponds to a later time at a later time point.

$$t_u(s_{in}, m, p) \geq t_u(s_{in}', m, p') \; \forall\, m \in M, p \in P, p \geq p', s_{in}', s_{in} \in S_{in} \tag{185}$$

The operation of each mixer is depicted by three time points, as previously discussed. Since three time points are used, a mixer cannot operate on two consecutive time points. To ensure this constraint (186) is used.

$$y(s_{in}, m, p) + y(s_{in}', m, p-1) \leq 1 \quad \forall\, m \in M, p \in P, p \geq p_1, s_{in}, s_{in}' \in S_{in} \tag{186}$$

Constraints (187) and (188) ensure that the washout starts directly after a mixer has finished operating. A mixer cannot operate without a washout taking place after the mix. Constraints (187) and (188) hold because each mixer can only mix one product at a time.

$$\sum_{s_{in}} y(s_{in}, m, p-1) \le y_w(m,p) \; \forall \; m \in M, p \in P, p > p_1, s_{in} \in S_{in} \tag{187}$$

$$\sum_{s_{in}} y(s_{in}, m, p-1) \ge y_w(m,p) \; \forall \; m \in M, p \in P, p > p_1, s_{in} \in S_{in} \tag{188}$$

At any time point in the time horizon the CIP tank can only send water to one mixing vessel and receive water from one mixing vessel. This is ensured with constraints (189) and (190). This is because only one washout can take place at a time. Furthermore each mixer is only allowed to mix one product at a time, this is ensured with constraint (191).

$$\sum_{m} ys_{in}(m,p) \le 1 \; \forall \; m \in M, p \in P \tag{189}$$

$$\sum_{m} ys_{out}(m,p) \le 1 \; \forall \; m \in M, p \in P \tag{190}$$

$$\sum_{m} y(s_{in}, m, p) \le 1 \; \forall \; m \in M, p \in P, s_{in} \in S_{in} \tag{191}$$

Objective function

The objective function for the model is the minimisation of the effluent water, given in constraint (192). This type of objective function can be used because the required production in the time horizon of interest is determined beforehand.

$$\min \sum_{p} \sum_{m} fe(m,p) \tag{192}$$

An example of the typical schedule generated with the final model is given below. For the example the four mixers were scheduled with the minimisation of wastewater as the main objective. Four different products were mixed and the time horizon was 24 hours. Within this time horizon two batches of a shampoo, three batches of a lotion, two batches of a deodorant and two batches of a cream needed to be produced. The mixing times are given in Table 4.

Table 4. Mixing times

	Mixer 1 (hr)	Mixer 2 (hr)	Mixer 3 (hr)	Mixer 5 (hr)
Shampoo	8	8	8	8
Lotion	5	4	5	4
Deo	7	6	7	5
Cream	12	11	12	10

In this example it was assumed that the amount of water used for the sanitising step was 500 l. The resulting schedule is given in Figure 10. The total amount of effluent from all the sanitising steps at the end of the time horizon was 500 l in total. In the figure all the water used for the first washout comes from the sanitising water. The dashed arrows in the figure show reused water entering a vessel from the CIP tank for a washout and the solid arrows show sanitising water going to the CIP tank for reuse later. The washout of mixer one after the first batch of shampoo uses fresh water and no sanitising water, since it is the first washout in the time horizon and there is no sanitising water available for reuse. At the end of the time horizon the sanitising water from the washout of mixer two, after the batch of cream, goes to effluent. This is because this is the last washout in the time horizon.

The important feature of the application of the methodology is that the plant can be scheduled while reducing the amount of effluent produced. Furthermore the final methodology can easily be applied to the current situation and be used for the scheduling of production in the mixing area, while taking reuse into consideration.

Using the above model the amount of water used in each washout is decreased by the amount of water used for the sanitising step. Depending on the type of washout used the amount of water saved per washout was between 22% and 55%. The exact figure could

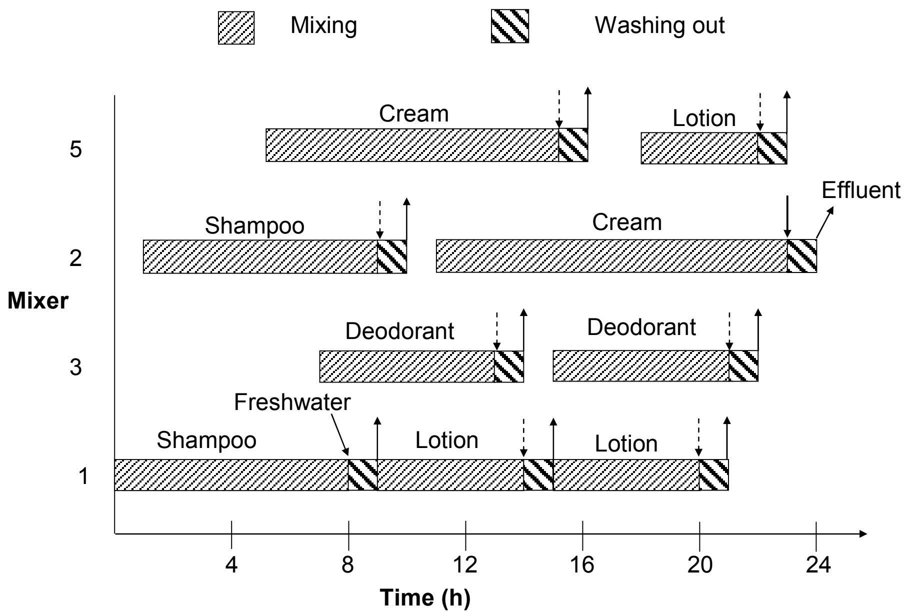


Figure 10. Production schedule produced from final model

not be given as the final amount of water used for sanitising had not yet been decided. Trials are still underway to determine the sanitising amount of water necessary.

The overall scheduling process is given in Figure 11. In the figure the first step is to define the number of batches that need to be produced and the time horizon of interest. The following step is to put this information into GAMS. GAMS using an appropriate solver, e.g. CPLEX, then solves the model and generates the text output of the schedule. The text output is then interpreted into a Gannt chart of the production schedule. Finally the mixing manager uses the schedule as the preliminary production schedule.

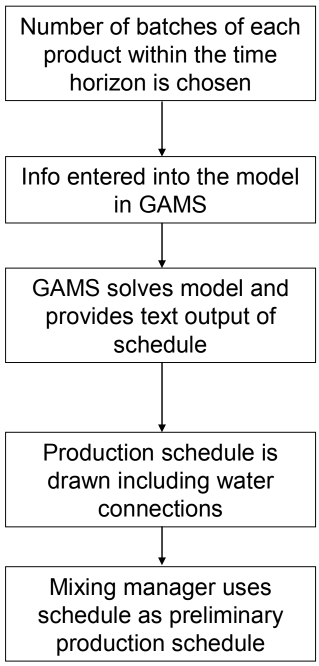


Figure 11. The overall proposed scheduling process at the industrial site

Observations on the plant indicated that there were many opportunities for saving water through process related changes, specifically with the water used for the sanitising step in a washout and the water used for temperature control. As part of the broader objective of water savings these opportunities were explored and subsequent changes were proposed and are currently under implementation. These opportunities are discussed are discussed as below.

4.3 Water Savings From Process Changes

4.3.1. Recycling of washout water from sanitising step

The chemical sanitising step in the washout sequence of a storage vessel or mixer was replaced by a hot water sanitising step. This was done because bacteria present in the mixer could build up a possible resistance to the chemicals used in the sanitising step. Prolonged exposure of micro-organisms to elevated temperatures provides the necessary means to kill the them. Due to the elevated temperature of the water used for sanitising this water should be free from detectable microbial content and readily available for reuse.

It is possible to directly reuse the water coming out of the sanitising step by directing the water back to the CIP water tank for reuse. This means that during the sanitising step there should be no effluent water as the water is constantly flowing back and forth between the CIP tank and mixer. Water at the end of the sanitising step is not discarded, but rather kept in the CIP tank for use in the first step of a washout in a subsequent washout. It is also noteworthy that the residence time for reusable water in the CIP tank should not exceed 6 hours.

The basic water flow during the washout cycle is shown in Figure 12. The recirculation of sanitising water to the CIP tank is controlled via two valves. During the first three steps of the washout procedure the valve in the return stream is closed and the valve to the drain is open. This ensures that water from the first three steps of the washout goes to the drain and is not sent to the CIP tank. During the sanitising step the valve to the drain is closed and the return valve is open, hence sending the sanitising water to the CIP tank for reuse. At the end of the washout the sanitising water returns to the CIP tank.

Two different heat sanitising steps were proposed. The first is where the sanitising step is a 90°C washout for 7 minutes. The second proposal is an 82°C washout for 30 minutes. During the sanitising step for both proposals the water used is recycled to the CIP tank. The current first three washout steps will be maintained. However, reusing sanitising water in the proposed manner is, in essence, independent of the sanitising step times. The only difference is in the amount of water saved. If the cycle time is reduced the amount of water saved is reduced.

Table 5 summarizes the savings that should be achieved with the reuse of the sanitising water.

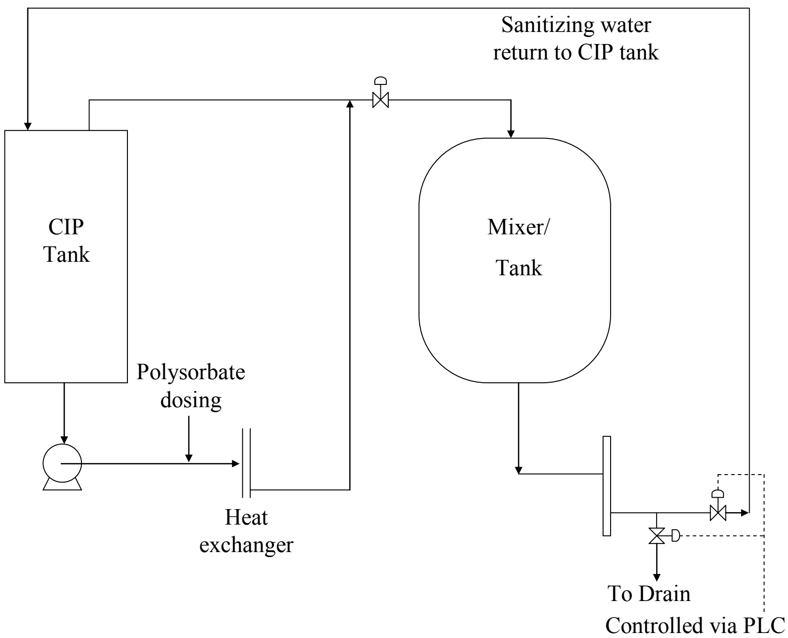


Figure 12. Process flow sheet for the reuse of sanitising water

The values given in Table 5 are given for the first proposed washout cycle and the second washout cycle. The savings reported in the table assume that all the sanitising water in the washout cycle will be reused. The table gives the amount of water used in each step of a washout.

Table 5. Water savings through sanitising water reuse

7 minutes 90°C	
Total other steps	2 500 l
Sanitising	700 l
Total Reused	700 l
Savings	**22 %**
30 minutes 82°C	
Total other steps	2 500 l
Sanitising	3 000 l
Total Reused	3 000 l
Water savings per washout	**55 %**

Based on the current washout figures the amount of water saved is 2% of the overall site water usage.

4.3.2. Water for temperature control in the pharmaceuticals area

The cold water source for both the petroleum jelly (PJ) mixers and the Olsa mixer, in the pharmaceutical mixing area, is municipal water. When it is required to reduce the temperature of the product in any one of the mixers municipal water is used. The hot water that is currently in circulation is discarded down the drain. This type of operation is undesirable for a few reasons. Firstly, the amount of water used and discarded is substantial, hence the cost of the water is high. Secondly, the hot water places unnecessary strain on the drainpipe system.

The discarded water can be captured by cooling the water and using this water as the cold water supply instead of municipal water.

The proposed cooling system is a three cooling tower system. One cooling tower will service each mixer and cool the water coming from the mixer exclusively. This is done to ensure that the cooling requirements of each mixer will be achieved and each mixer can operate independently of each other. There will be some losses in the cooling tower, this will be replenished by the municipal water supply.

Cooling water used by the Olsa mixer in 2005 accounted for 16.14% of the overall water used at the industrial site, as seen in Table 6. This trend is similar in 2006, where up until September of 2006, the mixer accounted for 12% of the overall water used on site, as seen in Table 6.

The amount of water used by the PJ mixers for temperature control in the month of November was 1 145 m^3. It is assumed that the monthly average in the year is 60% of that in November, hence for a year the amount of water used for temperature control on the PJ mixers is about 8 000 m^3, which is roughly 10% of the overall water used on site.

It is envisaged that the total amount of water saved on site through the installation of cooling towers for the Olsa and PJ mixers should thus be at least 20%.

Figure 13 shows the utilities loop and the proposed cooling tower addition. Important to note is that each mixer is independent from the others.

Table 6. Water usage and savings from cooling tower project

	Site	Olsa mixer
Total water used in 2005 (m^3)	86 973	14 038
Percentage used in 2005	100	16.14
Total water used in 2006 (end September) (m^3)	52 195	6 257
Percentage used in 2006	100	12

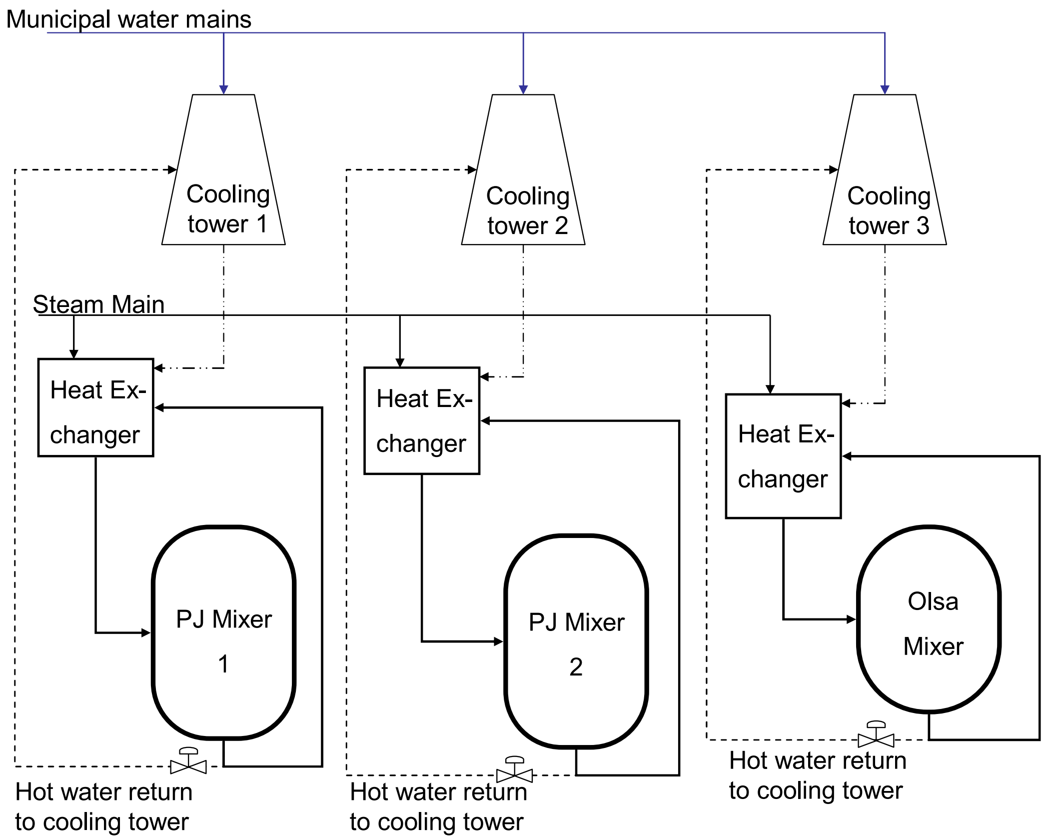


Figure 13. New utilities loop for the PJ and Olsa mixers

4.3.3. Other water saving ideas relating to operational changes

Apart from the two opportunities mentioned above, further opportunities for water savings were also identified. These opportunities would probably not yield as high a savings as the above opportunities, but are worthy of mention.

Batch washout

The washout water that would usually be going to the drain is directly recycled to the mixer. Hence the washout cycle produces no effluent during each part of the washout cycle and only at the end of the washout step. This type of operation would facilitate further water savings through scheduling, as it is more desirable to reuse water in fixed amounts. The basic idea is shown in Figure 14.

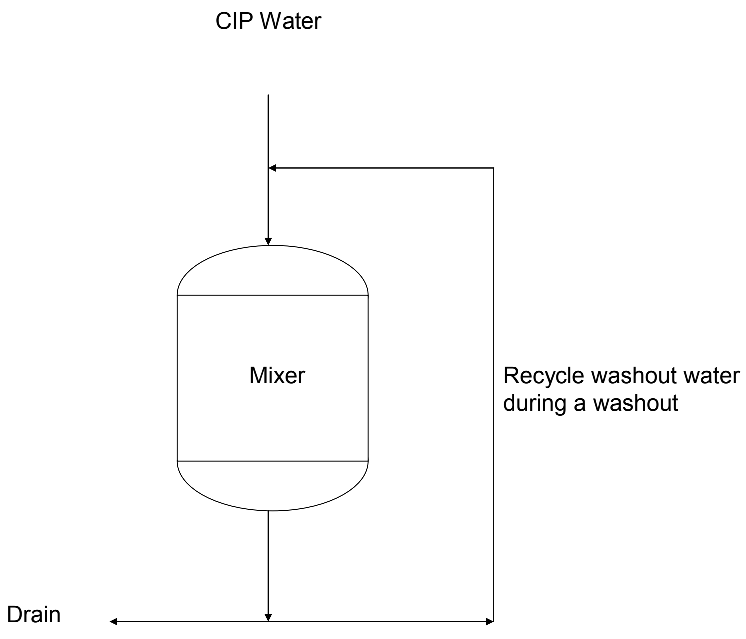


Figure 14. Batch washout of a mixer

Sprayball change

Currently fixed sprayballs are used during the washout. Replacing these with rotary sprayballs would mean that the washout is more effective. It is thus possible that one can reduce the amount of water used during a washout as a result of the higher efficiency.

Rotary type sprayballs have a greater water contact area and enhance the impinging effect of water on the vessel walls.

Use washout water from the oil phase vessel as pre-rinse

During the washout of the oil phase vessel, the water leaving the vessel can be sent though the sprayball of the water phase vessel. This will serve as the first rinse in the water phase vessel and the first rinse will not be required in the subsequent washout. This opportunity is shown in Figure 15.

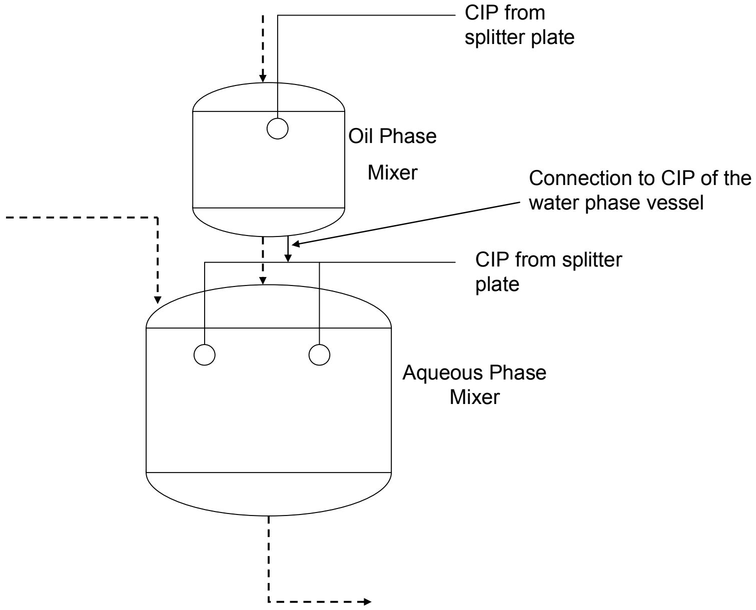


Figure 5. Water used from the oil phase mixer as a for a pre-rinse for the aqueous phase mixer

Reuse of washout water to clean the portable vessels

Water from a mixer or storage tank washout can be reused as washout water for a portable vessel. During the closing phases of the chemical washing step of a mixer/storage vessel there is virtually no product in the water, thus making this viable. This can either be done by directly sending the water to the water supply hose at the portable tank washout bay or it can be done by sending the water to a dedicated storage tank. This is shown in Figure 16.

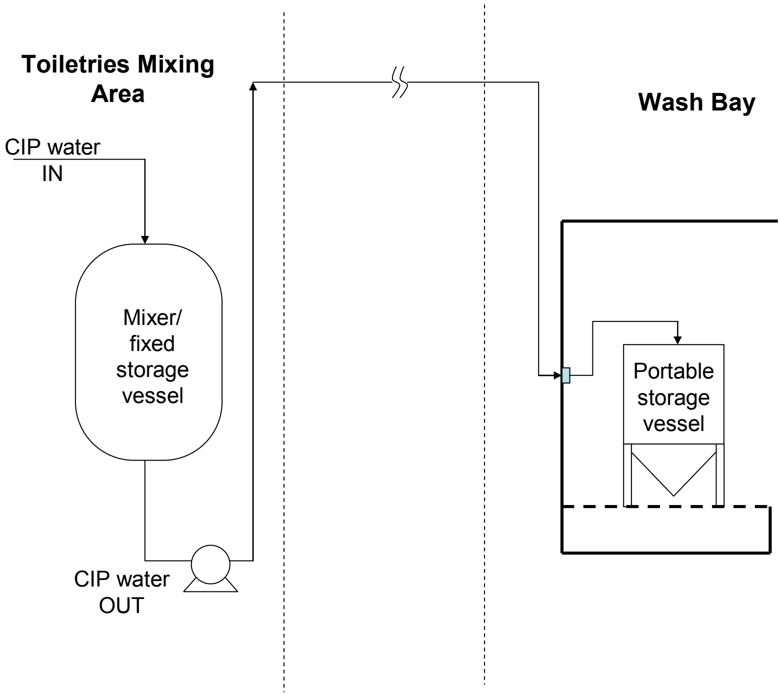


Figure 16. Reuse of washout water from the toiletries area for portable vessel washout

5. DISCUSSION AND CONCLUSIONS

Wastewater minimisation in batch processes is important due to the nature of the wastewater. Wastewater minimisation in batch processes has not been the focus of research in the past. Furthermore, existing methodologies are restricted to situations where there are only single contaminants present in a system. Multiple contaminant water systems are, however, more common in practice. Hence, what is needed is a process integration methodology that addresses wastewater minimisation in the multiple contaminant environment. The aim of this project was to develop process integration methodologies that minimise wastewater in batch processes with a focus on multiple contaminant wastewater.

Two mathematical methodologies were derived to minimise wastewater within batch processes. The first methodology dealt with multiple contaminant wastewater minimisation with, at most, a single storage vessel for wastewater storage. Noting that it is possible that there might be multiple storage vessels within the system, a second methodology that dealt with multiple contaminant wastewater minimisation with multiple storage vessels was derived.

A pharmaceutical production facility was identified and used to apply the derived methodologies to. The application of the derived mathematical methodologies to the industrial site was done in three steps. The first step involved the application of a single contaminant methodology to the operation. The first step gave insight into the operation and the data that was required. From the first step it was observed that product and wastewater compatibilities needed to be taken into account. Based on this, the multiple contaminant wastewater minimisation methodology with a single storage vessel was applied to the industrial site. This formed the second step of the application. During the application of the multiple contaminant model an important change came about in the sanitising method used. The chemical sanitising step was changed to a heat sanitising step. Based on this, a final model was derived in the final step of the application of the methodologies.

The final model schedules the production in such a manner as to maximise the amount of water that is reused, thus producing less effluent. The amount of water saved for each washout is dependent on the amount of water used for the sanitising step. The amount of water saved varies between 22% and 55%. The derived model finds practical application as it takes the current water usage into consideration. The output from the model is a production schedule. The production schedule shows the allocation of mixers to various products under the actual production requirements. Since water from the sanitising step goes to a central storage vessel, independent of the mixer, no extra pipe connections are needed to achieve water savings.

Apart from water savings achieved through the application of the model, further water was saved at the industrial site through process related changes. Reusing the sanitising water lead to a 2% savings of the overall water used on site. Capturing the water used for temperature control at the Olsa and PJ mixers at the industrial site leads to 20% savings in the overall water used on site (this currently under implementation). Further water savings ideas were also identified on the industrial site.

The application of the mathematical methodologies to the industrial site was successful. During the application of the methodologies to the industrial site it became apparent that in order to successfully apply the methodology one would have to tailor it to the operation of interest. The application of the methodologies is, however, limited due to the solution method. Currently the only means of solving the methodologies is by using GAMS. The usage of GAMS means that the user needs experience with GAMS and must be able to interpret the text output from GAMS.

However, due to the superstructure approach, the methodologies can be applied to many different types of operations. Provided the required data is known, a solution can be found. It is, however, important that the correct methodology be chosen for the operation of interest.

It was further observed during the implementation of the wastewater minimisation methodology at the industrial site that the water that was used for the first rinse of a washout contains high levels of product residue and no other contaminants. By changing the type of water used for the first washout from municipal water to deionised water, it should be possible to reuse this water as part of the formulation of a batch of a similar product. This would mean that the product residues that would normally be discarded will be recaptured, as is the water from the first washout. This observation would mean that the operation could possibly function in a manner that is tending towards zero effluent. To fully exploit this observation, one would have to derive a methodology that would schedule the operation and reusing water as part of product.

6. RECOMMENDATIONS

Many of the identified opportunities for water savings at the industrial site are currently under implementation. Furthermore, further water saving ideas have been identified. Further water savings through scheduling can only be achieved at the industrial site through the consideration of each step of a washout. This would then necessitate that the current model be modified to account for the added washout steps.

The application of the derived methodologies to other industrial opportunities would require the development of software that simplifies the steps necessary to find a final solution. Furthermore, since problem-specific information is required in each operation, the user of the methodology would require an in-depth understanding of the methodology. Therefore, it is recommended that for full scale industrial application of the derived methodologies further work be done on software development.

It is also recommended that future work be done on developing a zero effluent model, since it was observed that pharmaceutical operations generally produce wastewater containing product that can be reused. This would then allow any given operation to achieve a near zero discharge scenario and allows the recovery of expensive product. Currently more than 500 tons of product is dispensed with as effluent, which translates to more than R7 million in lost revenue. This figure is based on 6 batches/day and 20 kg of residue per batch for 300 days of operation per year and at R14 per kilogram product.

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