DESIGN OF MINIMUM WATER NETWORK FOR GLOBAL WATER OPERATION

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SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature

Name of Supervisor:

Position:

Date:

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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ABSTRACT

Water is key utilities in process industry. A reduction of this utility can reduce plant capital as well as operating cost. Though there are graphical techniques that often are use but mathematical modelling techniques can produce global optimal solution which means it best techniques to be used. In this paper, a new systematic design methodology has been developed for the water minimization involving multiple-contaminant systems that also feature maximum re-use water. In this study, the proposed model is developed based on linear programming (LP). The technique consists of four main steps, i.e. limiting water and energy data extraction, superstructure representation, mathematical formulation, and finally, result analysis. This technique is applicable to mass transfer based and non-mass transfer based (global water operations). The proposed methodology is mathematically rigorous and targets the minimum utility requirement satisfying for detailed design of the water allocation network. The model is successfully implemented on in two industrial case studies involving petroleum refinery and chlor-alkali plant. The proposed model also can guarantee the global optimal solution. Through this approach, the optimal design of the water network can be achieved.

ABSTRAK

Air adalah utiliti utama dalam industri proses. Pengurangan utiliti ini boleh mengurangkan modal loji serta kos operasi.Walaupun terdapat teknik-teknik grafik yang sering digunakan tetapi teknik-teknik pemodelan matematik boleh menghasilkan penyelesaian yang optimum global yang bermakna ia teknik-teknik terbaik untuk digunakan. Dalam kertas kerja ini, satu kaedah reka bentuk yang sistematik yang baru telah dibangunkan untuk meminimumkan air yang melibatkan pelbagai bahan pencemar sistem yang juga mempunyai penggunaan air semula yang maksimum. Dalam kajian ini, model yang dicadangkan dibangunkan berdasarkan pengaturcaraan linear (LP). Teknik ini terdiri daripada empat langkah utama, iaitu mengehadkan air dan tenaga pengekstrakan data, perwakilan mahastruktur, penggubalan matematik, dan akhirnya, analisis hasil. Teknik ini digunakan untuk pemindahan jisim dan bukan berasaskan pemindahan jisim (air operasi global). Kaedah yang dicadangkan adalah matematik yang ketat dan sasaran keperluan utiliti minimum yang memuaskan untuk reka bentuk terperinci rangkaian peruntukan air. Model ini berjaya dilaksanakan dalam dua kajian kes industri yang melibatkan penapisan petroleum dan loji klor alkali. Model yang dicadangkan juga boleh menjamin penyelesaian optimum global. Melalui pendekatan ini, reka bentuk rangkaian air yang optimum dapat dicapai.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

$Cd_{j,k}^{max}$	Concentration limit of contaminant *k* in water demand *j*
Cs_{k}^{max}	Concentration of contaminant *k* in water stream from source *i*
Cw_k	Concentration of contaminant *k* in fresh water
D_j	Water demand
FW_j	Fresh water supplied to demand *j*
$F_{i,j}$	Flow rate of water from source *i* demand *j*
H_2S	Hydrogen Sulfide
H_2O	Water
H^+	Concentration of hydrogen
Min	Minimum
S_i	Water source
WW_i	Waste from water source
%	Percentage

LIST OF ABBREVIATIONS

FW	Fresh water
GAMS	General algebraic modeling system
HDS	Hydrodesulfurization
LP	Linear programming
MTB	Mass transfer based
NLP	Non-linear programming
NMTB	Non-mass transfer based
ppm	part per million
WW	Wastewater

CHAPTER 1

INTRODUCTION

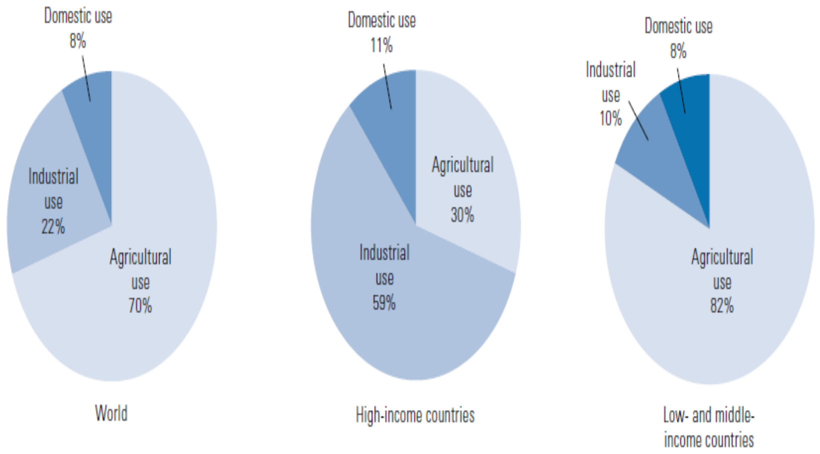
1.1 INTRODUCTION

Water is one of chemical substances in the world and it has chemical formula which is H_2O. Its molecule contains one oxygen and two hydrogen atoms connected by covalent bonds. Water usually in liquid condition but it also exists in earth as solid, gas, and vapour or steam.

1.2 GLOBAL WATER OUTLOOK

On the Earth, most of the surface is covered by water which is 70.9%, it is mostly can be found in oceans and other large water bodies. Water also can be found below ground in aquifers and in the air which consist of 1.6% and 0.001% of water, respectively. Surface water is hold by ocean about 97%, followed by 2.4% water locked in glaciers and polar ice and leaving only 0.6% of water available for human use from lakes, river and ponds (Natural Resources Final Report, 2010).

Nowadays water has become a very valuable resource for use in agricultural, industry and domestic sectors. Figure 1.1 shows the percentage uses of water in the world, high income countries as well as low and middle income countries.



(a) (b) (c)

Figure 1.1: Water usage in (a) the world (b) high-income countries (c) low and middle income countries

Source: The United Nations World Water Development Report (2003)

The figure shows that the highest use of water in industry is come from high income countries which consist of 59% followed by world 22% and low and middle income countries 10%. These statistics show that water is one of important material in industry. In industry water commonly uses in landscaping, cooling, and laundry, in kitchens and restrooms, and for over all processing needs, like fabricating, diluting, incorporating water into a product, and/or for sanitation needs within the facility.

Commonly freshwater is used for the process use in industry and the outcome of using freshwater will generated the wastewater. This wastewater is been treated in treatment facility to remove contaminant in order to meet the regulatory specification for wastewater disposal.

1.3 PROBLEM STATEMENT

Nowadays water has become an important resource for industrial activity, recreation and life in general. Water is vital in a number of processes in industry. It can be used product formulation, cooling, general plant service water, fire protection and water also can be use as a medium for extracting impurities from process stream. Water is becoming more and more scarce resource and it now have the potential to be limiting factor for agricultural and even for industrial development. The increasingly amount of fresh water uses in industry will also increase the cost of production at plant. The amount of wastewater been generated also will increase due to increasingly of fresh water. Over the past two decades, significant effort has been made to reduce the quantity of industrial wastes generated. Therefore this study is to propose a model to reduce the consumption of fresh water in industry and simultaneously reduce the waste water generated.

1.4 RESEARCH OBJECTIVE

To develop a new mathematical model for simultaneous targeting and design of minimum water network for global water operation.

1.5 SCOPE OF STUDY

There are two scope of study in this research which is:

a) Developing mathematical model for maximum water recovery.

b) Applying the optimization models on case studies to illustrate the effectiveness of the proposed model

1.6 RATIONALE AND SIGNIFICANCE

Water is one of key utilities in process industry. Water is used in industry as raw material or as medium heat transfer. Wastewater effluent from industry need to be treated before the water can be discharged to environment or be used in other process .By decrease the amount of fresh water supply into the plant, less wastewater been generated and this will decrease the time and money to treat the wastewater. Reduction of this utility can reduce plant capital as well as operating costs. Even though graphical methods are often preferred to provide insights through visualization, the tedious graphical has limitation when handling large scale and complex problems. By doing this research we can reduce amount of water that been uses in industry and in the same time we can reduce the amount of wastewater produce.

CHAPTER 2

LITERATURE REVIEW

2.1 A REVIEW ON WATER MINIMISATION

Water is one of the most important materials and mostly used as raw material in industries. Significant amount of water is required in some process like washing, stripping, and manufacturing process. Reduce amount of water used will reduce the cost of operational plant. Some researchers have been done to reduce water utilisation in batch process because batch process usually is used to produce high commercial chemical like pharmaceuticals and agrochemical which can generate highly toxic wastewater.

Wang and Smith, *et al.* (1995a, 1995b) proposed water minimisation technique for batch process by using water reuse and recycle opportunities. The authors developed a new graphical technique which can be use for semi-batch rather than strictly batch operations. However, the technique can only be applied to single contaminant system.

Another minimisation of water from batch process waste has been done by Grau, *et al.* (1996). The authors developed a mathematical model for waste minimisation with emphasis water generated during change over. This paper has three major limitations. First limitation is it only suitable or applicable to multiproduct batch process not multipurpose batch processes. Secondly, there exist an optimal production plan which sequencing of various campaigns is optimized to minimize changeover cost and lastly the procedure is based on the heuristics and the implies that optimality cannot be guaranteed.

Thokozani Majozi (2005) has done the research wastewater minimisation using central reusable water storage in batch plants. The author proposed a continuous-time mathematical formulation for fresh water and wastewater minimisation with consider a multipurpose batch plants with and without reusable water storage facility. Recycle and reuse opportunities is used to achieve the minimisation of wastewater. In this study, water using operation must include the data about the contaminant load, the water requirement, starting and finishing time to achieve desired target, maximum reusable water storage, and maximum inlet and outlet concentrations. All the datas must have in order to determine the minimum wastewater that can be achieve by exploitation of reuse and recycle opportunities. The word reuse in this research refer to the use an outlet water stream from process *A* to be use in another process *A'*, but for recycle is the outlet water stream in the process *A* will be used back in same process *A*. There are two superstructure have been design and the difference between this two superstructure is reusable storage tank. This mean one superstructure contains reusable storage tank which make water from reusable storage become an additional source to the system. The formulation that been develop is successful to reduce wastewater and fresh water with exploitation of water reuse and recycle opportunities and can be use in multipurpose batch-process but this technique only suitable for single contaminant media.

Wastewater minimization also is considered under uncertain operational condition which has been done by Suad A.Al-Redhwan *et al*. (2004). If operational condition and/or feedstock as well as product specification is changing it will change the wastewater flow rate and the level of contaminant, this because wastewater flow rate and contaminant is depend on the operational condition and/or feedstock and also product specification. So the optimal wastewater design should be able to accommodate this change. The stochastic optimization model that been proposed in this paper produce a flexible water network, which capable to accommodating uncertainties in operating temperature. There are three step methodology that been develop and used in this research. For the first step a deterministic optimization model is build, and this model will be test in order to find model that use minimum fresh water and in same time optimal wastewater reuse. The model will have a regeneration part if necessary to treat a wastewater before it can be use back if not the water will use directly without any treatment. Second step involves a sensitivity analysis in which uncertainty is introduced as maximum and minimum ranges in operational conditions. Last step is develop stochastic formulation based on two stage recourse problem which been discussed already in research done by Birge & Louveaux (1997) and Cheng *et al.*, (2003). This method is test on typical oil refinery wastewater network because refinery operation used a lot of water in their process. The result shows this method can be applied to any process industry.

2.2 WATER USING PROCESS

Water using process generally can be classified into two types that are fixed flow rate operations and fixed contaminant load operations. Fixed flow rate operations also known as non-mass transfer based (NMTB). Each inlet and outlet stream has a fixed flow rate but the concentration in the stream can be always changes. The flow rate entering and out the process do not need to be same but each stream can be treated independently. Fixed contaminant load operations are known as mass transfer based (MTB). According to Prakash and Shenoy (2005) MTB operation consists of process such as washing, scrubbing and extraction by using water as mass separating agent. In MTB the flow rate for inlet stream and outlet stream are necessarily equal and both stream are dependent each other. This mean if the demand flow rate is decrease the flow rate of the source should be decrease by the same amount.

CHAPTER 3

METHODOLOGY

This chapter discusses about the methodology of this research. The methodology is consist four stages or four steps which is first limiting water data extraction, follow by superstructure representation, mathematical formulation, and result analysis.

3.1 STEP 1: LIMITING WATER DATA EXTRACTION

The first step is to extract the limiting water data from a given water-using operations. The main data specifications are limiting contaminant data and flow rate for all available water sources and demands. The example of the contaminant is total suspended solid (TTS), total dissolved solid (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), hardness and also can be the specific contaminant for example the chemical in the water. Two case studies are discussed in this study. The first case is about petroleum refinery case study and the data is taken from Wang and Smith 1994. In this study specific contaminant and MTB operation is been applied.

3.2 STEP 2: SUPERSTRUCTURE REPRESENTATION

The second step is to develop a superstructure for the water network. This superstructure represents all possible connections among the water sources, water demands and wastewater. The Figure 3.1 shows a general water network superstructure.

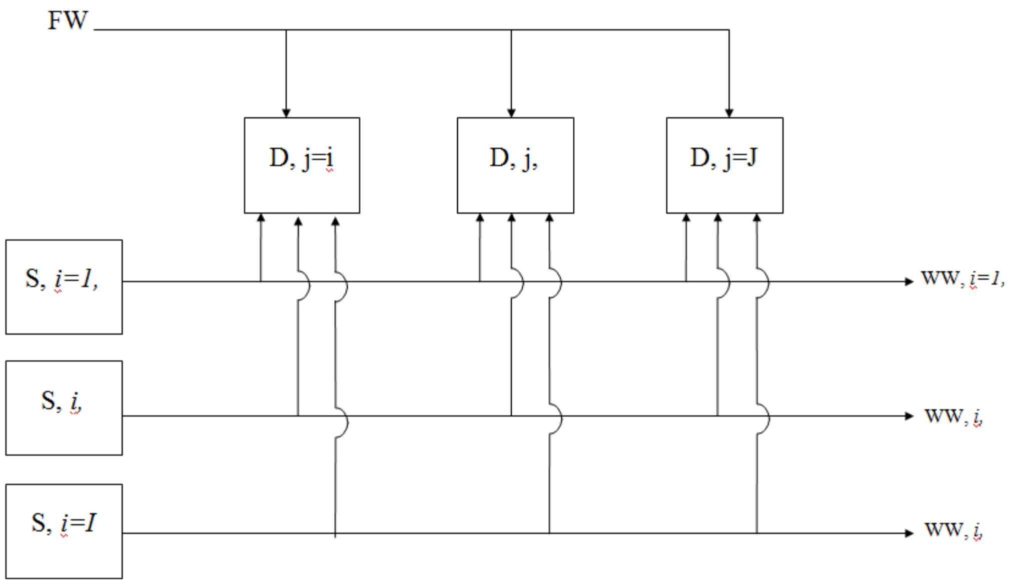


Figure 3.1: General water network superstructure

In the water operation process, the source of water can be the fresh water directly from supply or the water from other operation that be recycled into the water operation process. Water from the outlet stream from the operation can be discharged as waste water or be reused in other operation. All the possible connection in the system between fresh water, water sources and demand is represent in the Figure 3.1 general water network superstructure. This superstructure also showed the wastewater discharge for the system. The water flow rate of the source, demand, fresh water and wastewater is represent in superstructure as S_i, D_j, FW, and WW.

3.3 STEP 3: MATHEMATICAL FORMULATION

From data that has been extract in the first step, it will be use to construct a mathematical formulation. The mathematical formulation will be developing by using a commercial mathematical optimization software package which is general algebraic modeling system (GAMS).

In this section the mathematical formulation is develop to achieve the objective of this study to minimize the consumption of the fresh water in the water operation process. The mathematical formulation is develop based on the superstructure given in

Figure 3.1 and from the figure S_i and D_j is symbolize for water flow rate for source *i* and demand *j* with a maximum contaminant concentration for each contaminant *k*. $Cs_{i,k}$, is symbolized for contaminant concentration in the source and $Cd_{j,k}$ is symbolized for contaminant concentration in the demand. The flow of water from the source i to the demand j can be expressed in the form of $F_{i\,j}$ and for the flow of fresh water to demand j with concentration of *k*th contaminant in the fresh water Cw_k, can be shown as FW_j. WW_i refers the flow transferred from source *i* to waste without any maximum quality limit.

3.3.1 Assumption and limitation

There are few assumption and limitation been state in order to complete this study. The assumption and limitations are:

a) The contaminant concentration of demand and source for both case studies are fixed to their maximum value.

b) The fresh water is being assume pure without contaminant concentration

c) The water flow rate in water operations is constant and operates continuously.

d) The water system operates isothermally.

3.3.2 Objective function formulation

The objective of this study is to minimize the consumption of fresh water to the system, so the objective function is to minimize total amount fresh water been used in water operation process. The objective function can be express as:

$$\text{Min} \sum_{j} FW_j \tag{3.1}$$

3.3.3 Constraint formulation

Equation 3.1 represents the objective function of this study and it is depending on the constraints to use it. There are three types of constraint equations which are:

a) Water balance for each source and demand

The submission of the generated wastewater WW_i in the system for each source i and the flow rate of water from the source i to demand $_j$, $F_{i,j}$ must be equal to the amount of the water source, S_i that supply. This equation can be represent as:

$$WW_i + \sum_j FW_j = S_i \qquad (3.2)$$

For every demand $_j$, the fresh water that been supply FW_j and the water that been supply from the source Fij which been reused or recycle back must equal to desired water demand $_j$, D_j. The water balance for each demand j is:

$$FW_j + \sum_j F_{i,j} = D_j \qquad (3.3)$$

b) Demand contaminant load formulation

The contaminant load for demand j for *k*th contaminant is supply from many source for example fresh water FW_jCw_k and the water that be reused back from the source i, $F_{i,j}Cs_{i,k}$ that contains the *k*th contaminant. The mixed contaminant from fresh water and from the source must equal to the contaminant load for demand j. This relationship can be shown as:

$$FW_jCw_k + \sum F_{i,j}Cs_{i,k} \leq D_jCd_{j,k} \qquad (3.4)$$

c) Non-negativity constraints

A non-negativity variable means that the value of the variables must greater than zero or equal to zero. In this study the value of fresh water, wastewater generation and water flow rate from the source must be greater or equal to zero. Therefore this entire variable is known as non-negativity variable.

$$FW_j, WW_i, F_{i,j} \geq 0 \tag{3.5}$$

3.4 STEP 4: RESULT ANALYSIS

After the mathematical formulation is being developed, the simulation will be run to find where the formulation is correct. All the method can be illustrated in Figure 3.2.

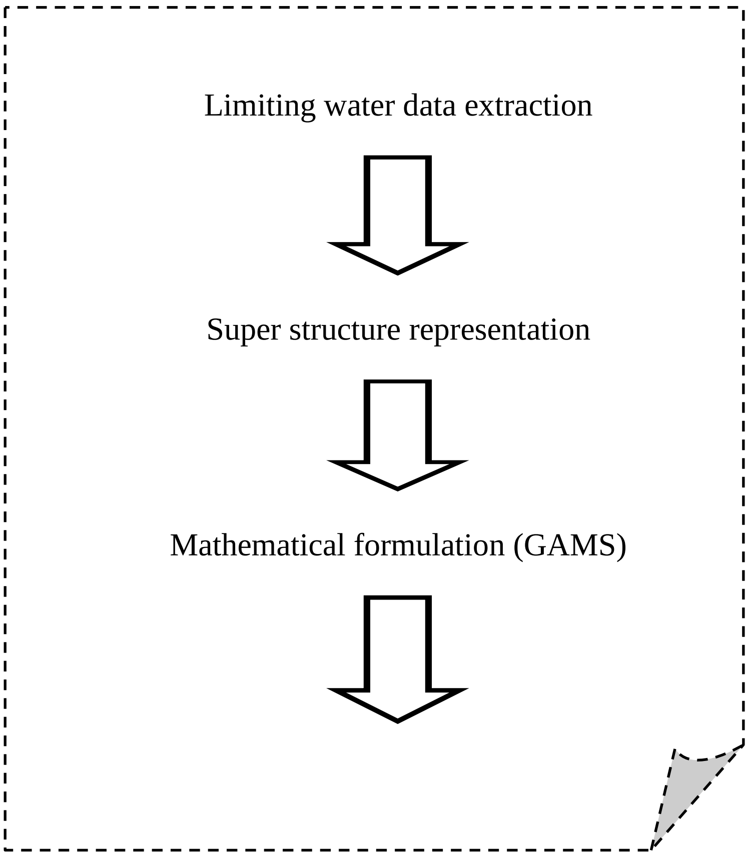


Figure 3.2: Flow work of methodology

CHAPTER 4

RESULT AND DISCUSSION

This chapter discusses about the result of total fresh water minimization in the water operation system. The models are applied on the industrial case studies involving petroleum refinery and chlor-alkali plant. . In the petroleum refinery case study, the result is validated with previous study. The result for case study petroleum refinery case study should be same with previous study. Second case study is industrial case study, which is Chlor-alkali plant water system. This study been use to see whether the propose methodology in this study can reduce total fresh water consumption in plant. The percentage of reduction fresh water will be calculated.

4.1 INDUSTRIAL CASE STUDY

In this study there are two cases that are discussed which first is petroleum refinery case study and chlor-alkali plant case study. The chlor-alkali plant is the industrial case study that use to see whether the propose model can reduce total consumption fresh water in the plant.

4.2 PETROLEUM REFINERY CASE STUDY

The petroleum refinery case study is the first case that will be discussed. This case study already was use in the previous study done by Mann and Liu (1999). The previous study also tries to minimize the fresh water using their approach. The result from this study using the proposed model will be compare to the study done by Mann and Liu (1999). The operating data, water demand data, and water sources for petroleum refinery case study is shown in the Table 4.1, 4.2, and 4.3.

Table 4.1: Operating data for petroleum refinery case study

Operation	Contaminant	Cmax,in (ppm)	Cmax,out (ppm)	Mass load (g/h)	Flow rate (t/h)
Distillation (stream stripping)	Hydrocarbon	0	15	675	45
	H2S	0	400	18000	−
	Salt	0	35	1575	−
Hydrodesulfurization (HDS)	Hydrocarbon	20	120	3400	34
	H2S	300	12500	414800	−
	Salt	45	180	4590	−
Desalter	Hydrocarbon	120	220	5600	56
	H2S	20	45	1400	−
	Salt	200	9500	520800	−

Source: Wang and Smith (1994)

Table 4.2: Water demand data for petroleum refinery case study

Demand description	Stream	Flow rate D_j (t/h)	Hydrocarbon Concentration (ppm)	H_2S concentration (ppm)	Salt concentration (ppm)
Distillation (stream stripping)	D_1	45	0	0	0
Hydrodesulfurization (HDS)	D_2	34	20	300	45
Desalter	D_3	56	120	20	200

Source: Wang and Smith (1994)

Table 4.3: Water source data for petroleum refinery case study

Demand description	Stream	Flow rate S_i (t/h)	Hydrocarbon Concentration (ppm)	H_2S concentration (ppm)	Salt concentration (ppm)
Distillation (stream stripping)	S_1	45	15	4000	35
Hydrodesulfurization (HDS)	S_2	34	120	12 500	180
Desalter	S_3	56	220	45	9 500

Source: Wang and Smith (1994)

This data is taken from Wang and Smith 1994 consists of three water using operation which is all MTB operation. The petroleum refinery case study is used to demonstrate the proposed model. The petroleum refinery case study contains three demands and three sources, it also involves three water operating system. The water operating system can be classified as distillation column using life steam injection, a hydrodesulfurization (HDS) unit, and a desalter. In this case, the contaminant concentration that been consider for water minimize are hydrocarbon concentration, H_2S and salt.

4.2.1 Water network for petroleum refinery process.

In this proposed model, linear programming (LP) model is been used to achieve objective function which is to minimize total amount of fresh water by solving the multiple contaminant system. LP model is used because of its capability to find the optimal value of a linear objective function for the multiple contaminant system that depends on linear constraints. Non-linear programming (NLP) do not be consider as one of the method to used because NLP is very dependent and cannot provide a global optimum.

The Figure 4.1 is shown the existing design of water network for petroleum refinery process. From the figure the amount of fresh water used is 135 t/h and this amount of fresh water is distributed to water using operation. For distillation the amount of fresh water needed is 45 t/h, 34 t/h for HDS, and 56 t/h for desalter. The amount of wastewater is 135 t/h which indicated that the amount of fresh water supply is been generated to wastewater. The existing water network design is not consider reusing or recycling the water into the system, but a new water network design will be consider it.

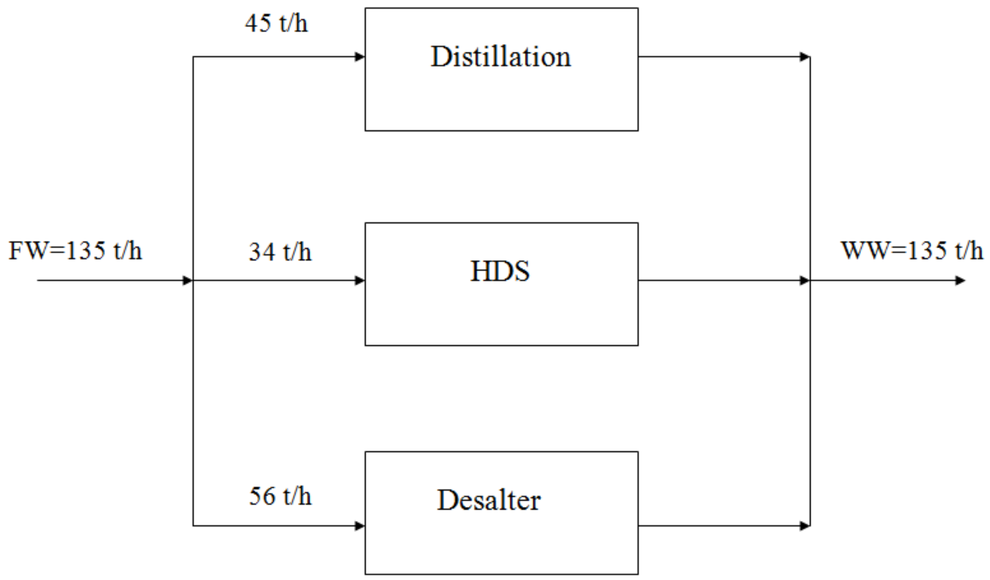


Figure 4.1: Existing design of water network for petroleum refinery process

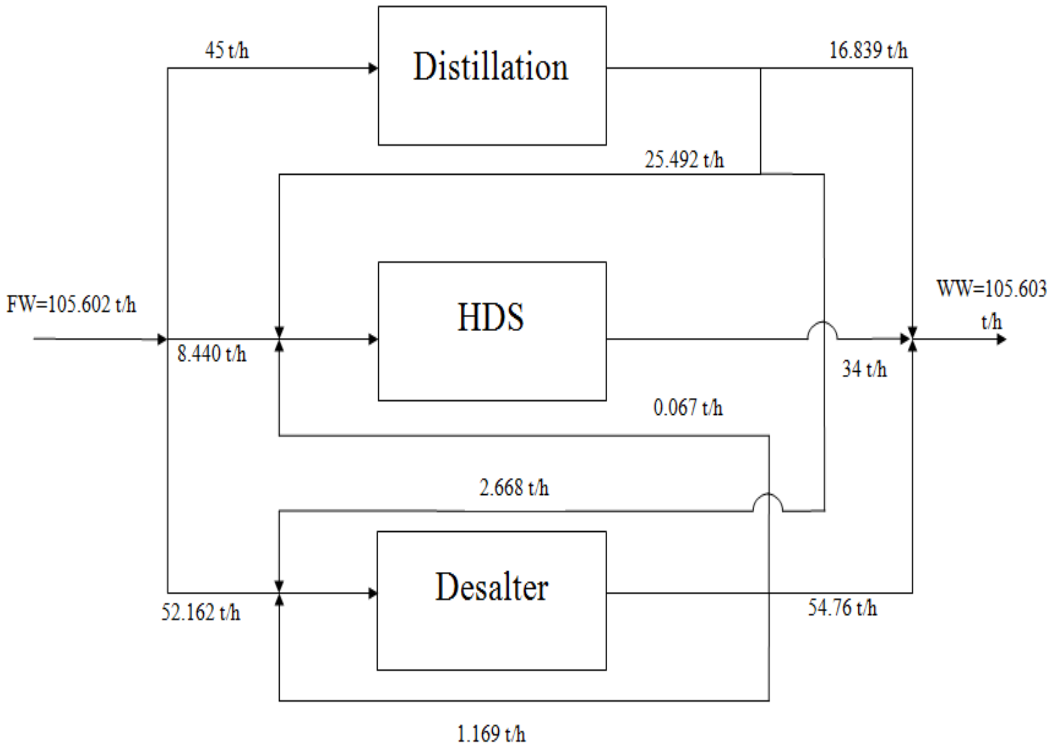


Figure 4.2: Minimum water network design for petroleum refinery process.

The result that come out from the commercial software General Algebraic Modeling System (GAMS) after the software been employed to find the solution shown that the amount of the fresh water been reduced into 105.602 t/h. The result is matched with previous study done by Mann and Liu (1999). The approach between this study with the Mann and Liu (1999) study is different each other but the result is same means that the proposed model in study is correct. The percentage reduction for fresh water and wastewater is 21.8%. The minimum water network design for petroleum refinery process can be refer to the Figure 4.2.

4.3 CHLOR-ALKALI PLANT CASE STUDY

4.3.1 Water usage in the Chlor-alkali plant

The fresh water supply to chlor-alkali plant is been divided three type of usage. The fresh water is use in process uses, non-process uses and domestic uses. The fresh water for process uses is use scrubber and production of demineralised water system. in the demineralised water system fresh water is use for many different process such as chemical and reagent preparation in precoat and reagent tank, use as feed water to boiler, catholyte tank and brine make-up water tank. The fresh water also has been use for regeneration at ion exchange in the brine. The acid hydrochloric is one of type acidic fume that cannot be disperse in the air, so the scrubber will use the fresh water to trap the acid hydrochloric before it disperse to the air.

The fresh water in non-process uses is use for many purposes such as washing at filling station and road tanker for NaOH and for HCl. In the non-process use the fresh water also uses for laboratory use, cooling tower, demineralised filter backwash and regeneration of demineralised water system. For domestic uses the fresh water is used for simple process such as toilet flushing, toilet pipes, office cleaning, wash basin and ablution. The Figure 4.3 showed the usage or distribution of fresh water in the chlor alkali plant.

The consumption of fresh water for process uses, non-process uses, and domestic uses is not same. The amount of fresh water supply to the plant is 28.82t/hr and the process uses demand the highest fresh water rather than non-process uses and domestic uses with the amount of 17.56 t/hr. The total wastewater that be generated in the plant is 9.44 t/hr. The demand of fresh water in the chlor-alkali plant and wastewater generated will be changeable according to the production of caustic soda and chlorine.

4.3.2 Water Balance

Figure 4.3 shows the water distribution in the plant. The water using process is been explained by drawing it in the term of water flow rate. The flow out of the water in the process is been represent by arrow come out from the box. The flow out of water generally will become waste but it also possible to become source for other process. The purpose of flow and contaminant balance is to estimate these requirement and limits from the existing operating data.

The water containing streams in the plant should already be explained using the flow sheet in the Figure 4.3 for water balance purpose. This guideline will not be use when a stream is completely outcast from the streams that will be included in the analysis.

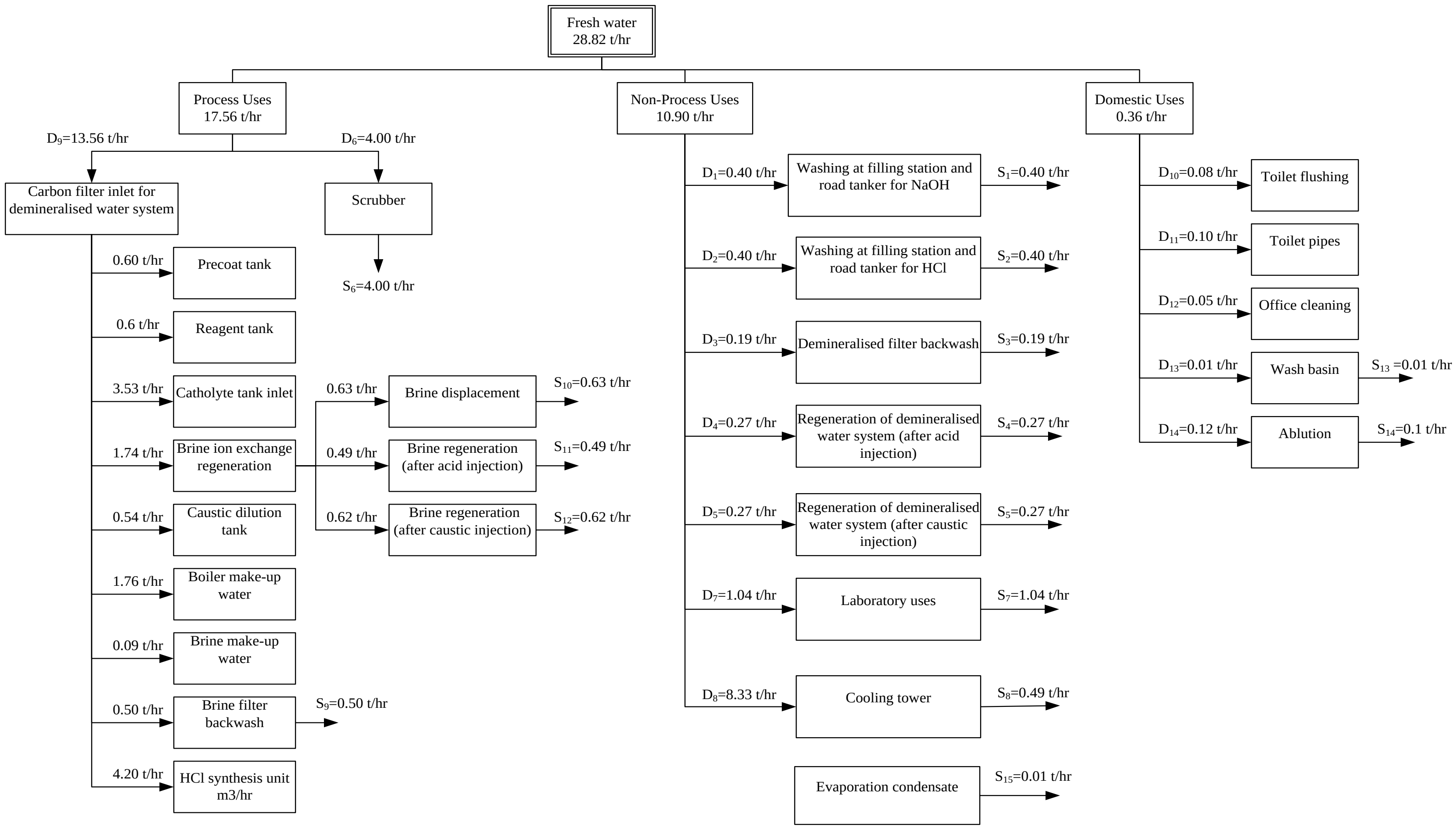


Figure 4.3: Water distribution in the chlor-alkali plant.

Source: Handani *et al.* (2010)

4.3.3 Limiting Water Data Extraction

The first step in the limiting water data extraction is to identify the source of water and the demand of water that can be use for integration. This step is done by set-up process material balance, line tracing and also isolating the appropriate source of water and demand of water that can be use for integration. The overall water network source and demand in the chlor-alkali plant is including in the limiting water data. The plant uses and domestic use also involve in determine the source and demand and finally the outcome result found that there are fourteen demand of water and fifteen sources of water. The MTB and NMTB operations are involved in this case study.

In this case study there three type of contaminant take into consideration which is pH, total dissolved solid (TDS), and hardness. The pH is values that determine the acidity or alkalinity of the solution by measure the concentration of hydrogen ions in the solution. According to Peavy *et al*. (1985) TDS can refers as the dissolved material in the water that can divided into organic and inorganic substances, meanwhile hardness can be explained as the concentration of multivalent cations in solution and the value of hardness is determine by measure the concentration of calcium and magnesium ions.

The limiting data for flowrate, and concentration of each contaminant for water demand and water source in the chlor-alkali plant is shown in the Table 4.4, 4.5, and 4.6.

Table 4.4: Flow rate for demands, D_j and sources, S_i water data for chlor-alkali plant.

D_j	Demand	Flow rate (t/hr)	S_i	Source	Flow rate (t/hr)
D_1	Washing at filling station and road tanker for NaOH	0.40	S_1	Washing at filling station and road tanker for NaOH	0.40
D_2	Washing at filling station and road tanker for HCl	0.40	S_2	Washing at filling station and road tanker for HCl	0.40
D_3	Demineralised filter backwash	0.19	S_3	Demineralised filter backwash	0.19
D_4	Regeneration of demineralised water system (after acid injection)	0.27	S_4	Regeneration of demineralised water system (after acid injection)	0.27
D_5	Regeneration of demineralised water system (after caustic injection)	0.27	S_5	Regeneration of demineralised water system (after caustic injection)	0.27
D_6	Scrubber	4.00	S_6	Scrubber	4.00
D_7	Laboratory uses	1.04	S_7	Laboratory uses	1.04
D_8	Cooling tower make-up water	8.33	S_8	Cooling tower blow down	0.49
D_9	Carbon filter inlet	13.56	S_9	Brine filter backwash	0.50
D_{10}	Toilet flushing	0.08	S_{10}	Brine ion exchange regeneration (brine displacement)	0.63
D_{11}	Toilet pipes	0.10	S_{11}	Brine ion exchange regeneration (after acid injection)	0.49
D_{12}	Office cleaning	0.05	S_{12}	Brine ion exchange regeneration (after caustic injection)	0.62
D_{13}	Wash basin	0.01	S_{13}	Wash basin	0.01
D_{14}	Ablution	0.12	S_{14}	Ablution	0.12
			S_{15}	Evaporation condensate	0.01

Source: Handani *et al* (2010).

Table 4.5: Contaminant concentrations data for water demands**,** $Cd_{j,k}^{max}$.

D_j	Demand	Type of water operation	pH	TDS (ppm)	Hardness (ppm)
D_1	Washing at filling station and road tanker for NaOH	MTB	7.5	65	17.1
D_2	Washing at filling station and road tanker for HCl	MTB	7.5	65	17.1
D_3	Demineralised filter backwash	MTB	7.5	65	17.1
D_4	Demineralised ion exchange regeneration (after acid injection)	MTB	7.5	40	17.1
D_5	Demineralised ion exchange regeneration (after caustic injection)	MTB	7.5	40	17.1
D_6	Scrubber	MTB	7.5	100	17.1
D_7	Laboratory uses	MTB	7.5	65	14.0
D_8	Cooling tower make-up water	NMTB	7.5	100	14.0
D_9	Carbon filter inlet	NMTB	7.5	60	14.0
D_{10}	Toilet flushing	NMTB	7.5	100	17.1
D_{11}	Toilet pipes	NMTB	7.5	65	17.1
D_{12}	Office cleaning	NMTB	7.5	65	17.1
D_{13}	Wash basin	NMTB	7.5	65	17.1
D_{14}	Ablution	NMTB	7.5	65	17.1

Source: Handani *et al* (2010).

Table 4.6: Contaminant concentrations data for water sources, Cs_k^{max}

S_i	**Source**	**Type of water operation**	**pH**	**TDS (ppm)**	**Hardness (ppm)**
S_1	Washing at filling station and road tanker for NaOH	MTB	10.8	30360	14
S_2	Washing at filling station and road tanker for HCl	MTB	2.5	704	16
S_3	Demineralised filter backwash	MTB	7.4	75	20
S_4	Demineralised ion exchange regeneration (after acid injection)	MTB	1.2	3300	14
S_5	Demineralised ion exchange regeneration (after caustic injection)	MTB	9.3	60	14
S_6	Scrubber	MTB	0.3	528	40
S_7	Laboratory uses	MTB	8.3	400	100
S_8	Cooling tower blow down	NMTB	6.9	3300	147
S_9	Brine filter backwash	NMTB	10.6	6579	14
S_{10}	Brine ion exchange regeneration (brine displacement)	NMTB	10.2	526	0
S_{11}	Brine ion exchange regeneration after acid injection	NMTB	0.02	396	0
S_{12}	Brine ion exchange regeneration after caustic injection	NMTB	13.6	1254	0
S_{13}	Wash basin	NMTB	7.7	60	20
S_{14}	Ablution	NMTB	7.7	60	20
S_{15}	Evaporation condensate	NMTB	11.1	76	0

Source: Handani *et al* (2010)

4.3.4 Chlor-alkali plant process

The chlor-alkali plant is the industrial case study which consists of MTB and NMTB operations. In this case there are fourteen demands and fifthteen sources. As shown in Figure 4.3, the fresh water is need for three major processes in the water system which is for process use, non-process use and domestic use. The higher consumption of fresh water is at process use.

In the chlor-alkali plant case study, there are three contaminants that be considered. The first contaminant is pH value of the water, second is total dissolved solid (TDS) and lastly hardness. The TDS and hardness are measure in the unit of part per million (ppm). The assumption is made state that the concentration of the contaminant in the fresh water is zero. This mean the fresh water is pure water. The data for the flow rate, concentration of contaminant for demand *j* and source *i* can refer to the Table 4.4, 4.5 and 4.6**.** All the data is inserting into the GAMS and the software is run to solve and provide the best solution to minimize the total fresh water used.

The concentration of contaminant in this study is in the unit of ppm. For the pH contaminant the value is not in the concentration value. The values of concentration for pH is determined by calculate the concentration of ion hydrogen (H^+) in the water. The concentration of ion H^+ are found using the equation 4.1:

$$-pH = \log_{10}(H^+) \tag{4.1}$$

Table 4.7 and 4.8 shown the value of concentration contaminant in the water demand and water source in the unit of ppm. This value is use in calculation by GAMS to find the best solution for minimum fresh water used in the chlor alkali plant

Table 4.7: The concentration of contaminant in the water demand

Demand Dj	Flow rate (t/hr)	pH (ppm)	TDS (ppm)	Hardness (ppm)
D1	0.4	3.16228E-08	65	17.1
D2	0.4	3.16228E-08	65	17.1
D3	0.19	3.16228E-08	65	17.1
D4	0.27	3.16228E-08	40	17.1
D5	0.27	3.16228E-08	40	17.1
D6	4	3.16228E-08	100	17.1
D7	1.04	3.16228E-08	65	14
D8	8.33	3.16228E-08	100	14
D9	13.56	3.16228E-08	60	14
D10	0.08	3.16228E-08	100	17.1
D11	0.1	3.16228E-08	65	17.1
D12	0.05	3.16228E-08	65	17.1
D13	0.01	3.16228E-08	65	17.1
D14	0.12	3.16228E-08	65	17.1

Table 4.8: The concentration of contaminant in the water source

Demand Si	Flow rate (t/hr)	pH (ppm)	TDS (ppm)	Hardness (ppm)
S1	0.4	1.5849E-11	30360	14
S2	0.4	0.003162278	704	16
S3	0.19	3.98107E-08	75	20
S4	0.27	0.063095734	3300	14
S5	0.27	5.01187E-10	60	14
S6	4	0.501187234	528	40
S7	1.04	5.01187E-09	400	100
S8	0.49	1.25893E-07	3300	147
S9	0.5	2.51189E-11	6579	14
S10	0.63	6.30957E-11	526	0
S11	0.49	0.954992586	396	0
S12	0.62	2.51189E-14	1254	0
S13	0.01	1.99526E-08	60	20
S14	0.12	1.99526E-08	60	20
S15	0.01	7.94328E-12	76	0

4.3.5 Water network design for chlor-alkali plant.

The chlor-alkali plant is used to prove that the mathematical modeling approach in this study is applicable to be used for both MTB and NMTB operations to minimize total fresh water at the global water-using operations. From Figure 4.3 process 1 to 7 for demand *j* are MTB operation which is in this process it consume fresh water and discharge fresh water and the amount of both fresh water and waste water is same. For process 8 to 14 is NMTB operation where in process 9, 10, 11 and 12 the process only consume the fresh water and for process 8, 13 and 14 the amount of fresh water consume and waste water discharged are not same. For the source *i*, the process from 1 to 8 are MTB operations and process 9 to 15 are NMTB operations. The water network for chlor-alkali plant after integration is shown in Figure 4.4.

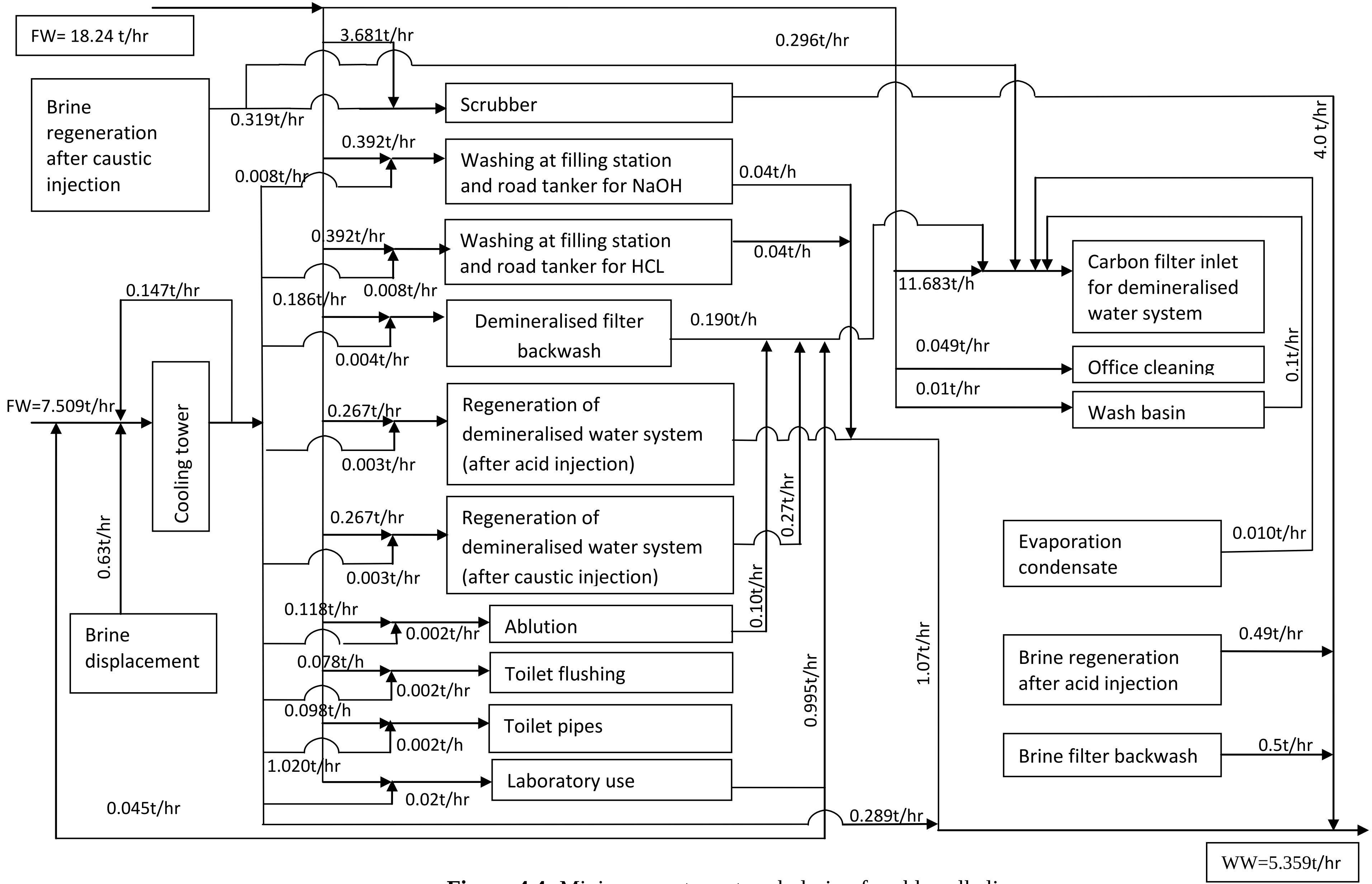


Figure 4.4: Minimum water network design for chlor-alkali

From the Figure 4.4 the water flows out the process is reused in another process and also recycle back into process. The wastewater from the cooling tower has been reused to many processes and almost half of it is use. Initially the water flow from the brine circuit is come out as a waste but after integration almost all the water is been reused into the process. The wastewater from brine displacement and brine regeneration is completely used as the supply water for another process. Total fresh water used in the process after integration is 25.749t/hr and the total wastewater generated is 5.359t/hr. The percentage of reduction of fresh water and wastewater is calculated using the equation 4.2 and 4.3.

$$\% \, Reduction = \frac{Fresh\ water\ before\ integration - Fresh\ water\ after\ integration}{Fresh\ water\ before\ integration} \times 100\% \qquad 4.2$$

$$\% \, Reduction = \frac{Wastewater\ before\ integration - Wastewater\ after\ integration}{Wastewater\ before\ integration} \times 100\% \qquad 4.3$$

The percentage reduction of fresh water in the chlor-alkali plant is 10.7% for percentage reduction of wastewater in the plant is 43.23%. The data is been summarise in the Table 4.9.

Table 4.9: The percentage reduction of fresh water and wastewater

Type of water	**Before integration (t/hr)**	**After integration (t/hr)**	**Reduction percentage (%)**
Fresh water	28.82	25.749	10.7
Wastewater	9.44	5.359	43.23

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

A mathematical optimisation approach for reduction of fresh water consumption in process plants have been developed. A proposed model is developiedbased on water network superstructure to achieve the objective of this study which is to minimum the fresh water. The proposed model also has been developing as linear programming (LP) model that can be used for MTB and NMTB operations. The proposed model has been used to solve water design network to minimum fresh water. The percentage reduction of fresh water and wastewater for petroleum refinery case is up to 21.8%, meanwhile for chlor-alkali plant the percentage reduction of fresh water is 10.7% and for wastewater is 43.23%.

5.2 RECOMMENDATION

The several recommendations proposed for future work**.** In future study, the concentration of contaminant in fresh water should be taking into consideration because there is possibility that fresh water will contain concentration contaminants. Second recommendation is to consider a regeneration process in the system. This is to increase the percentage of reduction of fresh water used in system.

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APPENDIX A

INSTRUCTION TO RUN GAMS FOR PETROLEUM REFINERY

```
Maximum water recovery and minimum fresh water consumption
* for a multiple contaminant problem
* through mathematical programming

SETS
  i   index for water source /1, 2, 3/
  j   index for water demand /1, 2, 3/
  k   index for contaminant /Hydrocarbon, H2S, Salt/    ;

PARAMETERS
  S(i) flowrate of water source in te per hour
  /1 45, 2 34, 3 56/

  D(j) flowrate of water demand in te per hour
  /1 45, 2 34, 3 56/;

PARAMETER Cw(k) freshwater concentration ;
  Cw('Hydrocarbon')=0;
  Cw('H2S')=0;
  Cw('Salt')=0

Table Cd(j,k) conc limit of contaminant k in water stream for demand j
        Hydrocarbon       H2S      Salt
   1    0                 0        0
   2    20                300      45
   3    120               20       200 ;



Table Cout(i,k) conc limit of contaminant k in water source i
```

```
     Hydrocarbon      H2S     Salt
  1   15              400     35
  2   120             12500   180
  3   220             45      9500 ;

FREE VARIABLE    Ftot    total freshwater flowrate ;
VARIABLES
  Fw(j)   flowrate of freshwater supply to demand j
  W(i)  unused portion of water source i (waste)
  F(i,j)  flowrate from source i to demand j ;

POSITIVE VARIABLES Fw(j), W(i), F(i,j);
EQUATIONS
  SUPPLY         define objective function
  MASSSOURCE(i)  mass balance for each source
  MASSDEMAND(j)  mass balance for each demand
  MASSLOAD1(j)    massload every internal demand for contaminant
Hydrocarbon
  MASSLOAD2(j)    massload every internal demand for contaminant H2S
  MASSLOAD3(j)    massload every internal demand for contaminant Salt;

  SUPPLY..
  Ftot =E= sum (j,Fw(j));

  MASSSOURCE(i)..
  W(i)+ sum (j,F(i,j)) =e= S(i);

  MASSDEMAND(j)..
  Fw(j)+ sum (i,F(i,j)) =e= D(j);

  MASSLOAD1(j)..
  sum (i, F(i,j)*Cout(i,'Hydrocarbon'))+ Fw(j)*Cw('Hydrocarbon')=l=
D(j)*Cd(j,'Hydrocarbon');
```

```
  MASSLOAD2(j)..
  sum (i, F(i,j)*Cout(i,'H2S'))+ Fw(j)*Cw('H2S') =l= D(j)*Cd(j,'H2S');

  MASSLOAD3 (j)..
  sum (i, F(i,j)*Cout(i,'Salt'))+ Fw(j)*Cw('Salt') =l= D(j)*Cd(j,'Salt');

MODEL MWRMC /ALL/;
SOLVE MWRMC USING LP MINIMIZING Ftot  ;
DISPLAY W.L, Fw.L, F.L, Ftot.L ;
```

APPENDIX B
THE RESULT FOR PETROLEUM REFINERY

GAMS Rev 237 WEX-WEI 23.7.3 x86_64/MS Windows 01/11/12 20:10:02 Page 6
G e n e r a l A l g e b r a i c M o d e l i n g S y s t e m E x e c u t i o n

---- 69 VARIABLE W.L unused portion of water source i (waste)

1 16.839, 2 34.000, 3 54.764

---- 69 VARIABLE Fw.L flowrate of freshwater supply to demand j

1 45.000, 2 8.440, 3 52.162

---- 69 VARIABLE F.L flowrate from source i to demand j

	2	3
1	25.492	2.668
3	0.067	1.169

---- 69 VARIABLE Ftot.L = 105.603 total freshwater flow rate

EXECUTION TIME = 0.047 SECONDS 3 Mb WEX237-237 Aug 23, 2011

APPENDIX C

INSTRUCTION TO RUN GAMS FOR CHLOR-ALKALI PLANT

```
Maximum water recovery and minimum fresh water consumption
* for a multiple contaminant problem
* through mathematical programming

SETS
  i   index for water source /1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15/
  j   index for water demand /1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14/
  k   index for contaminant /pH, TDS, Hardness/    ;

PARAMETERS
  S(i) flowrate of water source in te per hour
  /1 0.40, 2 0.40, 3 0.19, 4 0.27, 5 0.27, 6 4, 7 1.04, 8 0.49, 9 0.50, 10 0.63,
   11 0.49, 12 0.62, 13 0.01, 14 0.1, 15 0.01/

  D(j) flowrate of water demand in te per hour
  /1 0.40, 2 0.40, 3 0.19, 4 0.27, 5 0.27, 6 4, 7 1.04, 8 8.33, 9 13.56,
   10 0.08, 11 0.10, 12 0.05, 13 0.01, 14 0.12/;

PARAMETER Cw(k) freshwater concentration ;
  Cw('pH')=0;
  Cw('TDS')=0;
  Cw('Hardness')=0

Table Cd(j,k) conc limit of contaminant k in water stream for demand j
        pH          TDS     Hardness
   1   3.16E-08      65      17.1
   2   3.16E-08      65      17.1
   3   3.16E-08      65      17.1
   4   3.16E-08      40      17.1
   5   3.16E-08      40      17.1
```

```
  6    3.16E-08        100      17.1
  7    3.16E-08        65       14.0
  8    3.16E-08        100      14.0
  9    3.16E-08        60       14.0
  10   3.16E-08        100      17.1
  11   3.16E-08        65       17.1
  12   3.16E-08        65       17.1
  13   3.16E-08        65       17.1
  14   3.16E-08        65       17.1 ;

Table Cout(i,k) conc limit of contaminant k in water source i
        pH              TDS      Hardness
  1    1.58E-11        30360    14
  2    3.16E-3         704      16
  3    3.98E-8         75       20
  4    63.10E-3        3300     14
  5    5.01E-10        60       14
  6    501.19E-3       528      40
  7    5.01E-09        400      100
  8    1.26E-07        3300     1.47
  9    2.51E-11        6579     14
  10   6.31E-11        526      0
  11   955E-3          396      0
  12   2.51E-14        1254     0
  13   2.00E-08        60       20
  14   2.00E-08        60       20
  15   7.94E-12        76       0 ;

FREE VARIABLE    Ftot    total freshwater flowrate ;
VARIABLES
  Fw(j)   flowrate of freshwater supply to demand j
  W(i)  unused portion of water source i (waste)
  F(i,j)  flowrate from source i to demand j ;
```

```
POSITIVE VARIABLES Fw(j), W(i), F(i,j);
EQUATIONS
  SUPPLY        define objective function
  MASSSOURCE(i)  mass balance for each source
  MASSDEMAND(j)  mass balance for each demand
  MASSLOAD1(j)    massload every internal demand for contaminant pH
  MASSLOAD2(j)    massload every internal demand for contaminant TDS
  MASSLOAD3(j)    massload every internal demand for contaminant Hardness;

  SUPPLY..
  Ftot =E= sum (j,Fw(j));

  MASSSOURCE(i)..
  W(i)+ sum (j,F(i,j)) =e= S(i);

  MASSDEMAND(j)..
  Fw(j)+ sum (i,F(i,j)) =e= D(j);

  MASSLOAD1(j)..
  sum (i, F(i,j)*Cout(i,'pH'))+ Fw(j)*Cw('pH')=l= D(j)*Cd(j,'pH');

  MASSLOAD2(j)..
  sum (i, F(i,j)*Cout(i,'TDS'))+ Fw(j)*Cw('TDS') =l= D(j)*Cd(j,'TDS');

  MASSLOAD3 (j)..
  sum (i, F(i,j)*Cout(i,'Hardness'))+ Fw(j)*Cw('Hardness') =l=
D(j)*Cd(j,'Hardness');


MODEL MWRMC /ALL/;
SOLVE MWRMC USING LP MINIMIZING Ftot  ;
DISPLAY W.L, Fw.L, F.L, Ftot.L ;
```

APPENDIX D

THE RESULT FOR CHLOR-ALKALI PLANT

GAMS Rev 237 WEX-WEI 23.7.3 x86_64/MS Windows 01/11/12 11:06:14 Page 6

G e n e r a l A l g e b r a i c M o d e l i n g S y s t e m E x e c u t i o n

---- 94 VARIABLE W.L unused portion of water source i (waste)

1 0.400, 2 0.400, 4 0.270, 6 4.000, 8 0.289, 9 0.500
11 0.490

---- 94 VARIABLE Fw.L flowrate of freshwater supply to demand j

1 0.392, 2 0.392, 3 0.186, 4 0.267, 5 0.267, 6 3.681
7 1.020, 8 7.539, 9 11.683, 10 0.078, 11 0.098, 12 0.049
13 0.010, 14 0.118

---- 94 VARIABLE F.L flowrate from source i to demand j

	1	2	3	4	5
2	3.685877E-6	3.685877E-6	1.750792E-6	2.569527E-6	2.569527E-6

	1	2	3	4	5	6
2						4.00E-5
8	0.008	0.008	0.004	0.003	0.003	
12						0.319

+	7	8	9	10	11	12
2	9.583281E-6	7.737168E-5	1.308897E-4	7.033432E-7	9.214693E-7	

+	7	8	9	10	11	12

2

4.607346E-7

3			0.190			
5			0.270			
7		0.045	0.995			
8	0.020	0.147		0.002	0.002	9.847502E-4
10		0.630				
12			0.301			
13			0.010			
14			0.100			
15			0.010			

+	13	14
2	9.214693E-	8 1.105763E-6
8	1.969500E-4	0.002

---- 94 VARIABLE Ftot.L = 25.749 total freshwater flow rate

EXECUTION TIME = 0.047 SECONDS 3 Mb WEX237-237 Aug 23, 2011