MASS INTEGRATION FOR HAZARDOUS WASTEWATER REUSE WITH INCORPORATION OF ECONOMIC AND SAFETY OBJECTIVES

A Thesis

by

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ABSTRACT

With the development of society and the increasing population, the water crisis has been a severe problem for several regions in the world. Although various water-treatment technologies have been developed, water shortages continue to be on the rise. Due to the limited amount of available freshwater resources, maximizing the utilization of existing water resources has attracted much attention as a viable approach to addressing the water crisis. Among the factors contributing to the improvement of utilizing water, wastewater recycle plays a significant role. Wastewater is generally hazardous due to the presence of various pollutants. Therefore, wastewater reclamation and reuse can offer several economic, environmental, and health benefits.

In this study, analysis of the existing water stream network is conducted to develop potential sinks and sources of wastewater recycle. Mass integration is used as an overarching framework for optimizing water treatment and reuse. In addition to techno-economic analysis, assessments on the inherent safety and sustainability of the candidate solutions are conducted to evaluate the proposed wastewater reutilization networks.

Keywords: Hazardous Wastewater Reutilization, Mass Integration, Mass Exchange Network, Pinch Analysis, Inherent Safety, Sustainability

DEDICATION

This Thesis is dedicated to

my parents, Yang Zhu and Shizhen Cao

my sister, Ke Cao

and

My loved Lu Chen

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NOMENCLATURE

MEN	Mass Exchange Network
MI	Mass Integration
HEN	Heat Exchange Network
MSA	Mass-Separating Agent
MACD	Minimum Allowable Concentration Difference
HISEN	Heat-Induced Separation Network
WAP	Water Allocation Planning
ROI	Return on Investment
AEP	Annual Net Economic Profit
SWROIM	Safety Weighted Return on Investment
TCI	Total Capital Investment
ASP	Annual Sustainability Weighted Profit
ASSP	Annual Safety and Sustainability Weighted Profit
SASWROIM	Safety and Sustainability Weighted Return on Investment
WWROC	Wastewater Reverse Osmosis Concentrate

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CHAPTER I

INTRODUCTION

1.1 Background

Water resources are always playing a significant role in the development of the society. Not only because they are the most important foundation of basically all human's physiological activities, but also as a result of the large amount of fresh water consumption of agricultural and industrial activities. Although 70.8% of the Earth's surface is covered by water, 97% of it is salt water. In addition, only 3% is fresh water, and over two thirds of this is frozen in glaciers and polar ice caps. Most of the unfrozen freshwater is groundwater, which cannot be utilized directly. [1, 2] Therefore, available freshwater resources are extremely limited indeed. The global water resources have deteriorated rapidly over last few decades and the "water crisis" has become increasingly serious. On the one hand, the growth of global population is making the demands of fresh water increase, while the global hydrologic cycle is being affected by greenhouse warming, which makes the global water resources more vulnerable; on the other hand, the increasingly serious water pollution has eroded the large amount of water resources available.[3]

The reutilization of wastewater has drawn more and more people's attention. From the sustainability and safety perspective, reutilization of wastewater is extremely significant. Water is a necessary material for mankind to survive. Water pollution affects the long-term development of mankind, however, the reutilization of wastewater can eliminate or mitigate the hazards of wastewater from the root causes, so it is of great significance for the survival and safety of mankind. First, through the reutilization of wastewater, it is equivalent to producing a new available water resource, which alleviates the "water crisis" problem to some degree. Secondly, if polluted or untreated wastewater is discharged unproperly, clean fresh water will be eroded. In addition, the hazardous contents of wastewater endanger sustainability of environment and human's health significantly.

In the long run, it is not enough to carry out wastewater sanitation/treatment alone. Wastewater reutilization should also be put on the top of the agenda. Few areas of investment today have as much to offer the global shift towards sustainable development as sanitation and wastewater management. At the same time, there is growing recognition that societies can no longer afford to squander the water, nutrients, organic matter and energy contained in sanitation and other wastewater and organic waste streams. These water resources can, and should, be safely recovered and productively reused. [4]

1.2 Wastewater and Its Hazards

The water that has lost its original function is called wastewater. Wastewater is generated for many reasons, maybe due to the incorporation of new substances or because of changes in external conditions, resulting in deterioration of water and being unable to continue to maintain the original function of use. Depending on the source of wastewater, wastewater can be divided into these following categories:

- Industrial wastewater, including industrial site drainage (silt, sand, alkali, oil, chemical residues), cooling waters (biocides, heat, slimes, silt), processing waters, organic or biodegradable waste, organic or nonbio-degradable waste that is difficult-to-treat from pharmaceutical or pesticide manufacturing, extreme pH waste from acid and alkali manufacturing, toxic waste from metal plating, cyanide production, pesticide manufacturing, produced water from oil & natural gas production, solids and emulsions from paper mills, etc.
- Agricultural pollution, direct and diffuse.
- Human excreta (feces and urine), often mixed with used toilet paper or wipes; this is known as blackwater if it is collected with flush toilets.
- Washing water (personal, clothes, floors, dishes, cars, etc.), also known as greywater or sullage.
- Surplus manufactured liquids from domestic sources (drinks, cooking oil, pesticides, lubricating oil, paint, cleaning liquids, etc.).
- Urban runoff from highways, roads, carparks, roofs, sidewalks/pavements (contains oils, animal feces, litter, gasoline/petrol, diesel or rubber residues from tires, soap scum, metals from vehicle exhausts, de-icing agents, herbicides and pesticides from gardens, etc.).
- Groundwater infiltrated into sewage.

- Rainfall collected on roofs, yards, hard-standings, etc. (generally clean with traces of oils and fuel).
- Seawater ingress (high volumes of salt and microbes).

Therefore, due to the complexity of sources and composition of the wastewater, the hazards of wastewater are also varied.[5-8] Organic chemicals that contain N, S and halogen elements are one kind of common hazardous substance in wastewater, such as pyridine, quinoline, picoline, amino acid, amide, dimethylformamide, carbon disulfide, thiol, alkylthio, thiourea, thioamide, thiophene, dimethylsulfoxide, chloroform, carbon tetrachloride, chlorobenzenes, acid halides and dyes containing N, S, halogen, pesticides, pigments and their intermediates, etc. Heavy metals, such as copper, lead, cadmium, mercury, hexavalent chromium and so on, are also one kind of common highly hazardous pollutant.[9] Cadmium, lead and mercury can accumulate for a long time in humans and many animals, and are extremely toxic. Irreversible effects include damage to the nervous system, which includes the nervous system (affected by lead and mercury) or the kidneys (affected by cadmium) during adolescence and child development. Hexavalent chromium is highly toxic and easily absorbed by the body and can be absorbed by humans and animals through ingestion, inhalation or skin exposure. A low concentration of hexavalent chromium is also highly toxic, including for many aquatic organisms. It has been recognized to be toxic to the human respiratory system and can lead to nasal atrophy, ulcers, puncture of the nasal septum, changes in lung function, and other adverse effects on the respiratory system. In addition, hexavalent chromium can cause cancer in some cases. According to the properties and the way of causing damage, hazards in wastewater could be divided into following categories:

- Fire and explosions due to the formation and release of flammable gases during processing (e.g. CH_4, H_2).
- Vigorous chemical reactions caused by uncontrolled mixing of chemicals (e.g., if water is mixed with concentrated sulfuric acid) during preparation of reagents for wastewater treatment.
- Acute poisoning caused by various chemicals present in the wastes, used as reagents (e.g., gaseous Cl_2), or released during the treatment; a particular hazard is caused by the possible release of a number of poisonous gases, e.g., HCN, H_2S.
- Chronic poisoning by inhalation or ingestion of the chemicals used in wastewater treatment.
- Diseases caused by infectious agents (bacteria, viruses, protozoa, helminths and fungi) present in the raw domestic wastewater (mainly from human origin) and in agricultural wastes.
- Hazards related to entry into confined spaces – suffocation due to oxygen deficiency, poisoning (e.g. H_2S).

1.3 Wastewater Hazards Associated Incidents

For many years, work in the wastewater treatment field was considered the most hazardous, especially due to deaths involving confined space entry. This field is considered somewhat less hazardous today, but treatment plant workers still do experience health problems and deaths. These experiences occur in specific incidents involving chemicals in the sewer system and in regular work exposures throughout the plant and its processes.[10] According to records of National Fire Protection Association (NFPA), in 2006-2010, local fire departments responded to an estimated average of 260 fires at water utility properties per year. These fires caused an average of less than one civilian death, one civilian injury and $5.9 million in direct property damage annually. During the same period, fire departments responded to an estimated average of 590 fires at sanitation utilities per year. These fires caused an average of less than one civilian death, three civilian injuries and $13.7 million in direct property damage annually.

In addition, when the wastewater related hazards are discharged without treatment in a large amount, more and more incidents could happen and result in serious long-standing problems. Minamata disease was first discovered in Minamata city in Kumamoto prefecture, Japan, in 1956.[11] It was caused by the release of methylmercury in the industrial wastewater from the Chisso Corporation's chemical factory, which continued from 1932 to 1968. This highly toxic chemical bioaccumulated in shellfish and fish in Minamata Bay and the Shiranui Sea, which, when eaten by the local populace, resulted in mercury poisoning. While cat, dog, pig, and human deaths continued for 36 years, the government and company did little to prevent the pollution. As of March 2001, 2,265 victims had been officially recognized as having Minamata disease (1,784 of whom had died) and over 10,000 had received financial compensation from Chisso. By 2004, Chisso Corporation had paid $86 million in compensation, and in the same year was ordered to clean up its contamination. On March 29, 2010, a settlement was reached to compensate as-yet uncertified victims.[12-15]

The other disease due to hazardous wastewater is Itai-itai disease. It was the name given to the mass cadmium poisoning of Toyama Prefecture, Japan, starting around 1912. Itai-itai disease was caused by cadmium poisoning due to mining in Toyama Prefecture. The earliest records of mining for gold in the area date back to 1710.[16, 17] Regular mining for silver started in 1589, and soon thereafter, mining for lead, copper, and zinc began. The cadmium and other heavy metals accumulated at the bottom of the river and in the water of the river. This water was then used to irrigate the rice fields. The rice absorbed heavy metals, especially the cadmium. The cadmium accumulated in the people eating contaminated rice.[18] In 1992, the average annual health expense compensation for this disease was $6.55 million. Agricultural damage was compensated with $15.43 million per year. Another $5.47 million was invested annually to reduce further pollution of the river.[19]

1.4 Research Objectives

The objective of this research is to develop a systematic approach for designing wastewater treatment and reuse systems. Mass integration will be used as a framework for synthesizing and screening potential solutions. This research will focus on the utilization of mass integration and pinch-analysis technology of possible water streams to achieve the goals of improving safety, economic viability, and environmental sustainability. Specifically, the following objectives of the research will be addressed:

- Development of a mass-integration approach to selecting appropriate treatment technologies
- Identification of plausible wastewater sources and utilization sinks
- Determinations of optimal assignment of sources, treatment technologies, and sinks
- Screening of candidate solutions using economic, environmental, and safety considerations
- Application of the devised approach to a case study on wastewater utilization in a rubber and tire plant

CHAPTER II

LITERATURE REVIEW

2.1 Mass Exchange Networks

Since the last century, the increasingly serious environmental pollution and resource crisis has posed a threat to the survival of mankind. Therefore, cleaner production has become one of the popular research topics of scholars. Cleaner production includes three aspects: clean energy, clean products and clean process. In order to achieve cleaner production and prevent pollution, mass-exchange networks (MENs) had been proposed in the late 1980s and further expand into mass integration (MI). The MEN technology focuses on the mass flow in the process, and it can effectively minimize waste of the process, providing strong support for cleaner production. The MEN technology plays an important role in the realization of cleaner production in industries.

Through the study, El-Halwagi and Manousiouthakis found that there is a striking similarity between the MEN and heat exchange network (HEN) at the system level. Then, the idea of systematically synthesizing optimal reuse networks for waste reduction was brought out by El-Halwagi's introduction of the problem of synthesizing mass-exchange networks (MENs) in 1989.[20, 21] After this, there have been many articles published in the area of MENs. The main objective of synthesizing a MEN is systematically identifying a cost-effective and feasible network of mass-exchange units that can selectively transfer certain species from a set of rich streams to a set of lean streams (mass-separating agents (MSAs)).[22] Later, several pollutant reduction problems had been discussed. El-Halwagi used the MENs he designed to address the problem of how to optimize process and apply the new MENs to current existing systems in a cost-effective way. El-Halwagi and Manousiouthakis have studied the mass exchange network synthesis problem, including the regeneration of the lean stream and proposed the method of systematically solving the synthesis problem based on the concept of the minimum allowable concentration difference (MACD). Since all the previous studies focused on the problem of the physical mass exchange network, in 1992, El-Halwagi and Srinivas combined the mass transfer equation with the chemical reaction equilibrium and studied the mass exchange network accompanying the reaction.[23] They studied the MEN of the side reaction, and later, they took account of the inevitable heat exchange during the mass exchange process. They then discussed the exchange network synthesis issue that considers both mass exchange and heat exchange at the same time and obtained the optimal mass exchange temperature between the streams and the corresponding optimal network.

Since the heat separation agent is in direct contact with the stream and has obvious advantages in terms of environmental protection compared with the mass separation agent, El-Halwagi et al. introduced the synthesis of the heat-induced separation network (HISEN) and then used phase change instead of heat exchange to achieve the mass separation, such as through the crystallization process and other operations to remove pollutants. In order to reduce waste generation at the core of the process, El-Halwagi proposed the idea of waste interception and allocation to form an integrated waste set up, a complete solution framework for simultaneous treatment approach of gas and liquid wastes.[24] In the papers "*Synthesis of mass exchange networks*" and "*Automatic synthesis of mass-exchange networks with single-component targets,*" El-Halwagi et al. talk about design and analysis of MENs with a single transferable pollutant.[20, 25] Then, MENs with multiple pollutants,[21, 26] regeneration of MSAs,[27, 28] simultaneous waste reduction and energy integration,[29] chemically reactive separations,[23, 30] fixed-load removal,[31] total cost minimization,[32] flexible performance and controllable MENs were studied.[33, 34]

Later, El-Halwagi et al. systematically put forward the tools and strategies of mass integration based on the mass exchange network and gradually established a mass integration framework.[35-37] Mass integration focuses on the global distribution of mass, including the utilization and recycling of materials, the interception of substances in the process, chemical conversion, segmentation and mixing, and changes in the operation units, etc., providing a broader perspective on handling the environmental and other issues.

The MENs technology analyzes the existing waste streams or contaminated streams (rich streams) first, then through various mass exchange operations, such as absorption, desorption, adsorption, extraction, filtration and ion exchange, to contact with the other stream (lean stream), resulting in a mass exchange network that allows it to selectively process waste products, with constraints of mass balance, safety, or minimum costs, so that targeted pollutant or contaminant are removed. Other common terms in MEN technology are as follows.

Rich streams refer to streams in the process that are rich in specific substances. For pollution prevention, the specific substances could be pollutants or wastes. Lean streams receive the selected substances, which can be streams in the process or mass separating agents (MSA) outside the process, such as adsorbents, extractants, etc.

Mass exchangers refer to mass transfer operating units that use mass separation via direct contacting. Mass exchange operations include absorption, desorption, adsorption, extraction, ion exchange and so on.

The sink/generator operations are based on the calculation of flow rate or concentration of the flows to adjust them for optimization. These changes include changes in temperature or pressure, replacement of units, changes in catalysts, replacement of raw materials, changes in reactions or solvents, etc.

Interception is the use of separation techniques to adjust the concentration of target material in rich streams, so that they can be accepted by the lean streams. This operation is mainly achieved by using MSAs.

The operation of the generator covers the flow rate or concentration of the entering or leaving confluence by changing the latter's operation. These changes include changes in temperature or pressure, replacement of units, changes in catalysts, replacement of raw materials or products, changes in reactions or substitution of solvents, etc.

Recycle refers to the design of routes from the source to the sink. Each sink has constraints on flow rate and concentration. If the source stream satisfies these constraints, it can go directly to the sink; if the source stream does not satisfy these constraints, then it needs to be preprocessed by means of segmentation, blending or interception to make it suitable for the recycle.

In order to avoid an infinite mass exchange in mass transfer, a minimum value is set between the operating concentration and the equilibrium concentration of the stream, which is called the minimum allowable concentration difference (MACD). The minimum allowable concentration difference can generally be used as an optimization variable.

The goal of MSA technology is usually to achieve the lowest total annual cost, which includes operating costs (primarily the cost of MSAs) and fixed investment costs (primarily equipment costs for various mass separation units). MEN technology is widely used in feedstock pretreatment, product separation and refining, and the recovery of useful substances in the chemical industries. Recently, application of MEN technology has focused mainly on waste minimization and cleaner production in various industrial processes.

2.2 Wastewater Reutilization and Minimization via MENs

Material reutilization is one of the most effective and significant approaches to save raw material. Many scholars conducted an in-depth study on the MENs of special materials, such as the reutilization and minimization of wastewater.

Target identification of achievable minimum fresh water usage is the threshold of water reutilization design. A rigorous graphical approach was introduced by El-Halwagi to solve this kind of issues.[38] Mathematical analysis of the whole system and dynamic programing techniques were utilized to develop the systematic characteristics and conditions. Then they would be expressed graphically for segregation, locating the pinch point, mixing, and direct recycle. However, direct recycle may not be achievable due to some unavoidable causes, such as unacceptable high concentration level of impurities. Gabriel and El-Halwagi introduced an approach which integrated material reutilization and interception together via a source-interception-sink framework and mathematical program.[39] Ponce-Ortega and El-Halwagi also introduced a muti-objective mathematical programming approach to integrate wastewater treatment processes to water reutilization network optimization.[40]

Wang and Smith addressed the case of MENs with a single lean stream (water) for wastewater minimization.[41, 42] They applied the pinch technique to wastewater treatment issues and formed a systematic water-pinch technique.

Alva-Argaez achieved the minimization of wastewater by a decomposition scheme for the optimization of a superstructure model that includes all the possible features of a design under the scenario that the flow rate of the rich streams are constant.[43]

Castro introduced the concept of multiple pinches to prevent designing networks that do not lead to minimum cost distributed effluent treatment systems. He used mass problem tables, limiting composite curves and water source diagram, to maximize the water reutilization. Two different situations are considered, re-use and regeneration re-use for single contaminants. For re-use, three different methods of targeting are presented, one of them being simultaneously a design method. For regeneration re-use, he presented the first known algorithm for targeting minimum water consumption in all possible situations. The targeted flowrate is then used to design the mass-exchange network that almost always features splitting of operations.[44]

In order to overcome the deficiencies of the previous methods, Savelski and Bagajewicz established a superstructure model for water operations and used mathematical programming to determine the optimal water network structure.[45] They illustrated necessary conditions of optimality for single component water-using networks in process plants. These necessary conditions correspond to the optimal water allocation planning (WAP) problem that considers wastewater reuse on the basis of a single contaminant and where. The objective of WAP is to minimize the total water intake.

2.3 Pinch Analysis

Pinch analysis is a methodology for minimizing the energy consumption of chemical processes by calculating thermodynamically feasible energy targets and achieving them by optimizing heat recovery systems, energy supply methods and process operating conditions. It is also known as process integration, heat integration, energy integration or pinch technology.

Traditional methods of improving the process are limited by a number of unavoidable drawbacks that block the way in which the actual situation is modeled or what can be done and are shown below:

- A lot of inaccurate results due to the oversimplified model for general cases, however, different cases have various characteristics that do not fit the general model
- The solution adopted evolved from the earlier scenarios and is outdated, which is not reliable for different plant sites nowadays
- Complicated mathematical formulas may not be globally solvable and will only result in a locally optimal solution or require more work load

Bodo Linnhoff and his colleagues, under the supervision of Dr. John Flower, put forward the heat exchange network optimization design method based on the research results of their predecessors in the late 1970s and gradually developed it into a methodology of energy synthesis in chemical processes. Their research showed the existence in many processes of a heat integration bottleneck, 'the pinch', which laid the basis for the technique, known today as pinch-analysis.[46]

Pinch-analysis technology can be used not only for new plant design, but also for energy-saving transformation of existing plants. In the meantime, in recent years, it has gradually been applied to the energy-saving retrofit of old devices with low retrofit investment but better energy-saving purposes. In terms of goals and methods, these two fields are different. The application of pinch-analysis technology in new designs can result in savings in both energy and equipment investment, 30-50% reduction in operating costs and 10-20% savings in fixed equipment investment. In the optimization of existing plants, it is possible to reduce operating costs by 20-30%. Because of minimal equipment upgrades, this investment can be recovered in 1-2 years. Many projects in thousands of companies in the world have adopted the pinch-analysis technology and achieved very good economic benefits. Pinch-analysis technology can be used not only for energy saving, but also can be used to lift the "bottleneck" to solve environmental pollution problems.

Water pinch technology is an application of pinch technology in water systems and is a technological breakthrough in water systems design by process integrated engineering design technology. It can be used in the optimization of water-using systems to increase wastewater reuse rate. The technology was proposed by Y.P. Wang and Robin Smith in the United Kingdom in the late nineties of the last century and is conceptually integrated in the quality of the water system operation.[42] The core idea of water pinch technology is to maximize the amount of water used and the concentration of contaminants in the effluent, to identify the bottlenecks in design problems and to predict the minimum amount of water used in the design. As with the heat exchange network design, the water reuse process integrates to determine a water pinch, except that the water pinch is based on the concentration of a critical impurity while the heat exchange network is based on temperature. Therefore, the water pinch technology can be simplified as a mass transfer process from the impurity-rich stream to the water stream.

In 1996, Paul Tripathi stated that pinch-analysis technology is a powerful tool for the integration of mass transfer or heat transfer process, and then he applied the pinch-analysis technology in a wastewater minimization design in a paper mill.[47] In the same year, Polly pointed out that the design of the partial change of water utilization network would increase the water-reuse rate greatly.[48] After the integration process, the pinch point shifted accordingly and the bottleneck problem was solved at the same time.

In 1998, Kuo and Smith introduced a new method for the identification of regeneration opportunities.[49] Both regeneration reuse and recycling were addressed. The new method overcame the difficulties encountered with previous methods and is also complemented by methods to predict the number of regeneration and final effluent treatment units. This allows the implications of decisions made on regeneration for final effluent treatment to be more clearly understood. Fresh water usage and wastewater generation can be minimized through reuse and the appropriate use of regeneration.

Feng and Seider introduced a new network structure in which internal water mains are utilized. The structure simplified the piping network, as well as the operation and control of large plants involving many water-using processes; this included petrochemical or chemical complexes.[50] Then Wang proposed a design methodology for multiple-contaminant water networks with single internal water main. A new concept of ‘water-saving factor’ is proposed. Emphasis is placed on the location of the first internal water main, which is related to the maximum water-saving potential. The paper is accompanied by several case studies to illustrate the methodology. According to these case studies, water networks with just one internal water main determined by the presented method can clearly reduce water consumption, approaching the minimum water consumption target.[51]

The current shortage of fresh water resources and energy supply has become one of the limiting factors in economic growth. For the typical process industries such as the petroleum and chemical industry, the pinch point analysis method can be used to diagnose the water and energy consumption of the process system to find out the optimal possibilities of the process. Therefore, the application of pinch point analysis technology in mass exchange networks, heat exchange networks and water networks can bring enormous economic and social benefits to the development of the economy. A large number of existing facilities show that the use of pinch point analysis technology to guide the transformation or design of specific process systems can reduce the consumption of public works and initial investment costs, the implementation method is simple, with obvious advantages and broad application prospects.

CHAPTER III

PROBLEM STATEMENTS

The chemical process industries nowadays are capital intensive and operating on a large scale, consume a large amount of raw material, and discharge a lot of waste at the same time. For example, the rubber factory in Thailand in this study consumes a lot of fresh water and discharges a great deal of hazardous wastewater.

The objective of this research is to develop a systematic approach for designing wastewater treatment and reuse systems. Mass integration will be used as a framework for synthesizing and screening potential solutions. This research will focus on the utilization of mass integration and pinch-analysis technology of possible water streams to achieve the following goals: improving safety, economic viability, and environmental sustainability. Specifically, the following objectives will be addressed:

- Development of a mass-integration approach to selecting appropriate treatment technologies
- Identification of plausible wastewater sources and utilization sinks
- Determination of optimal assignment of sources, treatment technologies, and sinks
- Screening of candidate solutions using economic, environmental, and safety considerations

- Application of the devised approach to a case study on wastewater utilization in a rubber and tire plant

As shown in Figure 1, the first part of this research was to study the existing water utilization system and analyze possible sources and sinks. The existing system can be determined by analyzing the water balance of a specific factory or other industrial facilities. Based on the analysis, potential sources and sinks were identified for the optimization. The optimization results were varied due to the number of sources and sinks, as well as the optimization objectives. It is necessary to investigate as many potential sources and sinks as possible, and properties of these streams.

Once the study of the existing system was completed, the wastewater segregation was finished based on properties of wastewater streams. Then according to the requirements of different sinks, proper treatments for wastewater were selected to reach those requirements. Depending on optimization objectives, like minimizing the usage of fresh water and wastewater discharge, a detailed optimized wastewater reutilization was proposed. The last step was to conduct an evaluation on environmental sustainability, safety, and economy for the proposed reutilization network of wastewater.

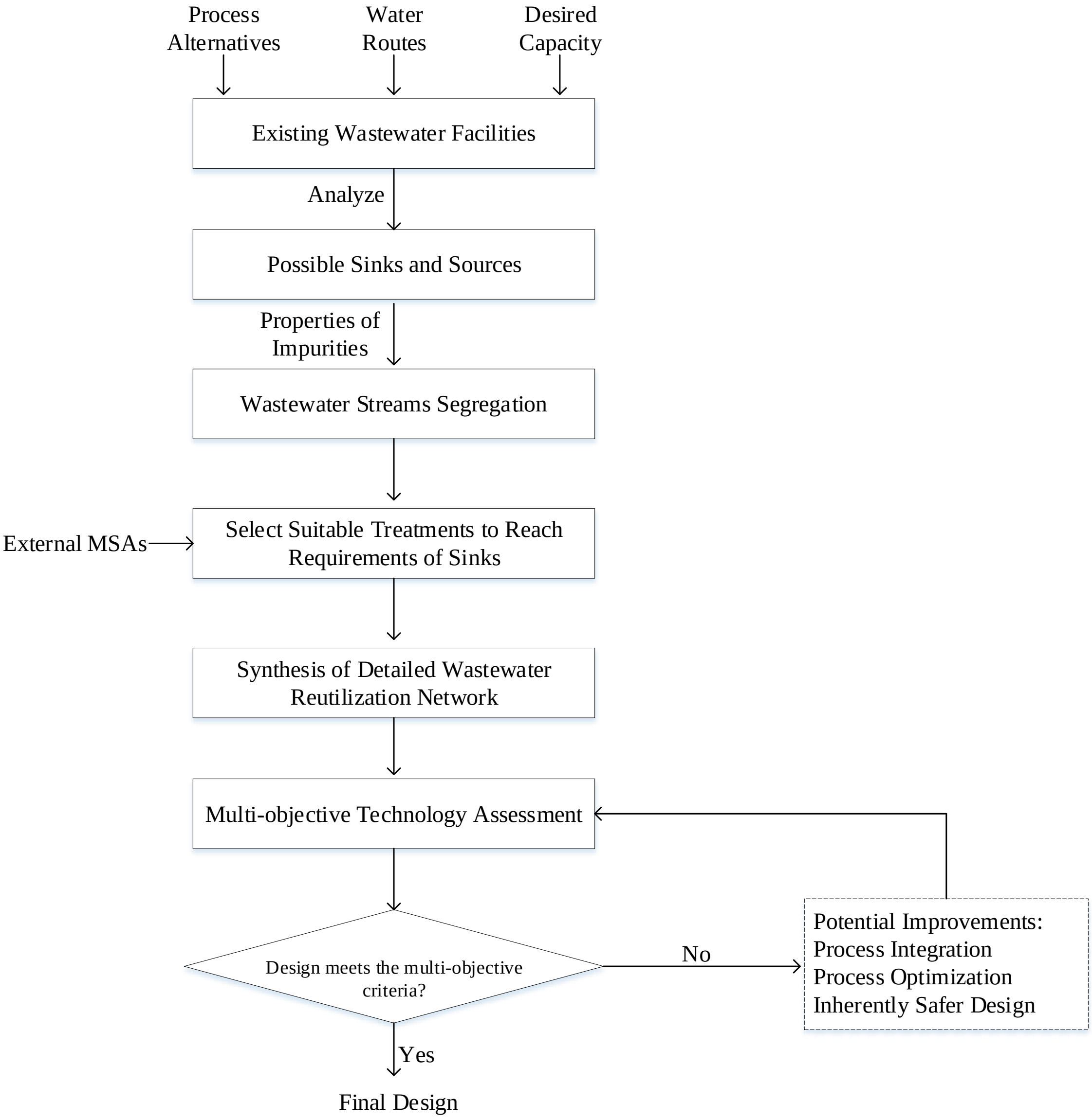


Figure 1. Framework of mass integration of hazardous wastewater reuse network.

CHAPTER IV

METHODOLOGY

4.1 Process Integration

To achieve the objectives in terms of minimal energy consumption, minimal cost and minimal environmental pollution in a process industry plant, the best approach was to integrate and optimize the entire system as an integral whole. A novel and systematic technique to approach the process design problems was to use process integration including process synthesis and process analysis.[22] The first priority of this approach was to consider the entire process network as a whole in terms of process framework input and output.

Process synthesis was in accordance with the provisions of the system performance, in accordance with the restrictions of the sytem, and in accordance with the provisions of the objectives of the optimal combination. Process synthesis involves the configuration of interactive and connected processes consisting of individual process elements. Therefore, structure generation and system optimization include separating or combining sequential flows, calculating and analyzing operation variables, comparing agents and chemicals, selecting units (reactors, flashers, heat exchangers, etc.) to meet certain requirements. In order to achieve specific goals, it was necessary to modify the system through process synthesis, such as select proper process inputs and outputs and determine the process structure and components of the process. The process synthesis problem is described in Figure 2. A.

The other fundamental part of the process integration, which was process analysis, divides the entire process into several components as a complement to the integration of individual process elements with individual performance evaluation. Therefore, once the process is synthesized or the alternatives are modified, the detailed characteristics of the process (such as temperature, flow rate, composition, and heat load) were studied as well. These technologies involved mathematical models, empirical prediction functions, and computer-aided process simulation tools. In addition, predicting pilot performance and confirming experimental data also had some overlap with process synthesis. The process analysis problem is described in Figure 2. B.

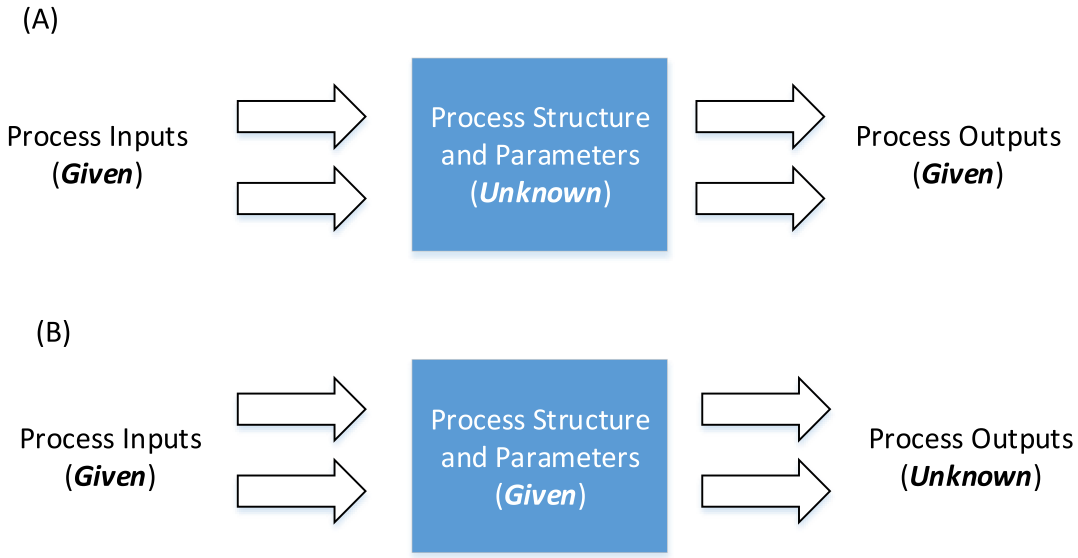


Figure 2. (A) Process synthesis problems. (B) Process analysis problems. (Adapted from [22])

Therefore, as we can see both process synthesis and process analysis are fundamental parts that make up process integration. While process synthesis and process analysis focus on different parts of process integration, respectively.

For different scenarios, detailed process integration could be varied. However, the framework of process integration has been summarized, and the process integration was conducted by following the sequence as shown below:[22]

1. Task Identification

Task identification is the fundamental step of process integration. This step determines the specific and "actionable" tasks that is needed to be achieved through process integration. The tasks should be reasonable, clear and based on the consideration of the input to the process. In addition, specific output, properties of products and economy should be considered.

2. Targeting

Targeting is the objectives of the proposed process integration. It refers to the identification of performance benchmarks ahead of detailed design. Targeting is aiming at the entire system rather than the individual component. It not only guides the designer in determining the true benchmarks for the process, but also saves time, effort and cost of implementation. Targeting clearly states the boundaries of the process integration and potential parameter that can be reached. However, specific approaches, techniques or other solutions will not be clarified in the targeting part.

3. Generation of Alternatives (Synthesis)

It is necessary to obtain all configurations of interest since there is a large number of alternative possible solutions. More importantly, generating possible alternatives will ensure the designer access the optimal solution of specific objectives.

4. Selection of Alternatives (Synthesis)

After embedding the appropriate alternatives for a process with suitable generative elements, it is beneficial to identify the best solution from among the possible alternatives. Algebra, graphics and mathematical optimization software can be used to verify the choice of the optimal solution.

5. Analysis of Selected Alternatives

The aim of this step is to elaborate the selected alternatives. With the help of evaluation on environmental sustainability, safety, economy and other benchmarks, it is convenient to verify the selected optimum solutions. In addition, once an alternative is generated or a process is synthesized, its properties, characteristics (e.g., flowrates, compositions, temperature, and pressure) and outputs could be predicted using analysis techniques.

The main advantage of process integration is to consider a system as a whole (i.e. integrated or holistic approach) in order to improve their design and/or operation. In contrast, an analytical approach would attempt to improve or optimize process units separately without necessarily taking advantage of potential interactions among them.

Process integration can be generally classified into two branches. The mass integration of hazardous wastewater reutilization system in this research belongs to the former one. Mass integration is a systematic methodology that provides a fundamental understanding of the global flow of mass within the process and then employs this understanding to identify performance targets and to optimize the allocation, separation, and generation of streams and species. Wastewater minimization, one of the primary objectives in this work, could be achieved via mass integration.

4.2 Mass-Exchange Networks

As El-Halwagi explained in the book,[22] the mass-exchange network synthesis problem can be stated as follows: Given a number N_R of rich streams (sources) and a number N_S of MSAs (lean streams), it is desired to synthesize a cost-effective network of mass exchangers that can preferentially transfer certain undesirable species from the rich streams to the MSAs. Given also are the flowrate of each rich stream, G_i, its supply (inlet) composition ysi, and its target (outlet) composition y_{i}^{t}, where i = 1, 2, ..., N_R. In addition, the supply and target compositions, x_{j}^{s}, and x_{j}^{t} , are given for each MSA, where j = 1, 2, ..., N_S.. The flowrate of each MSA is unknown and is to be determined so as to minimize the network cost.

The candidate lean streams can be classified into N_{SP} process MSAs and NSE external MSAs (where $N_{SP} + N_{SE} = N_S$). The process MSAs already exist on plant site and can be used for the removal of the undesirable species at a very low cost (virtually free). The flowrate of each process MSA that can be used for mass exchange is bounded by its availability in the plant, for example, as shown in Equation below:

$$L_j \leq L_{\mathrm{j}}^{c} \quad \mathrm{j} = 1,2,\ldots,N_{sp}$$

where L_{j}^{c} is the flowrate of the jth MSA that is available in the plant. On the other hand, the external MSAs can be purchased from the market. Their flowrates are to be determined according to the overall economic considerations of the MEN.

For a mass-exchange network, it is possible to segregate the streams according to their corresponding properties and characteristics once the target is set. And at the same time, possible sinks could also be figured out for source streams to enter. The most important part in this step is to design the optimal way(s) for those streams flow from sources to sinks, while achieving objectives in terms of economy, safety, and environmental sustainability. In this work, the objectives are minimum fresh water usage and wastewater discharge, enhancement in safety and lower the cost of operation. The mass-exchange network synthesis problem could be described as below in Figure 3.

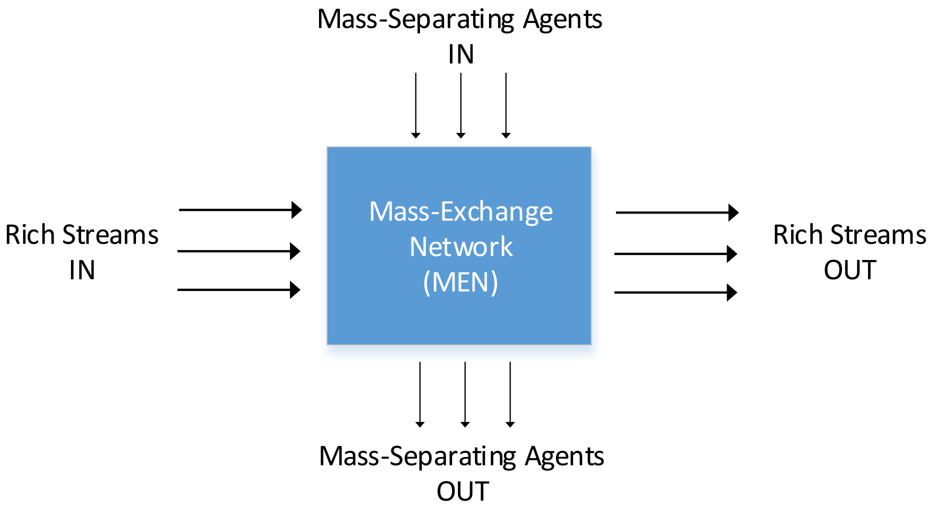


Figure 3. Schematic representation of the mass-exchange network synthesis problem. (Adapted from [20])

Based on the fundamentals of chemical analysis, mass balance and equilibrium are the most significant functions in mass-exchange network synthesis problems. The system can be divided into process sinks and process sources. Process sinks are units that accept species, so streams that flow out of sinks will be reversed to the source which supplies those species. In this regard, changing design operations that affect flow and concentration will in turn manipulate sinks. In this way, usage of raw materials could be reduced by using the recycled streams from the other outlet streams via the proposed mass-exchange network. In addition, the amount of discharge of outlet streams would be reduced at the same time. This also means the target of minimizing fresh water usage and hazardous wastewater discharge would be achieved. On the one hand, cost-effectiveness of raw materials is improved due to the reduced amount of fresh water. On the other hand, reduced amount of hazardous wastewater also eliminates the source of hazards to some degree.

4.3 Direct-Recycle Networks

To achieve the targets and mass-exchange network, El-Halwagi also explained how to construct direct-recycle networks:[22, 38] consider a process with a number $N_{Sources}$ of process sources (e.g., process streams, wastes) that can be considered for possible recycle and replacement of the fresh material and/or reduction of waste discharge. Each source, i, has a given flow rate, W_i, and a given composition of a targeted species, y_i. Available for service is a fresh (external) resource that can be purchased to supplement the use of process sources in a number N_{Sinks} of process sinks. The sinks are process units (e.g., reactors, separators, etc.) that can accept recycled streams. Each sink, j, requires a feed whose flow rate, G_{j}^{in} , and an inlet composition of a targeted species, Z_{j}^{in}, must satisfy certain bounds on their values. These bounds are described by the following constraints as shown below:

$$G_{\mathrm{j}}^{min} \leq G_{\mathrm{j}}^{in} \leq G_{\mathrm{j}}^{max} \quad \text{where j} = 1,2,\dots,N_{Sinks}$$

Where G_{j}^{min} and G_{j}^{max} are given lower and upper boundaries on admissible flowrate to unit j.

$$Z_{\mathrm{j}}^{min} \leq Z_{\mathrm{j}}^{in} \leq Z_{\mathrm{j}}^{max} \quad \text{where j} = 1,2,\dots,N_{Sinks}$$

Where Z_{j}^{min} and Z_{j}^{max} are given lower and upper boundaries on admissible compositions to unit j.

When fresh resources are used in process sinks, like fresh water in this study. A pure fresh, which means $Z_{\mathrm{j}}^{min} = 0$, could be used as the boundary:

$$0 \leq Z_{\mathrm{j}}^{in} \leq Z_{\mathrm{j}}^{max} \quad \text{where j} = 1,2,\ldots,N_{Sinks}$$

Based on the fundamentals of chemical analysis, mass balance and equilibrium are the most important rules in building a direct-recycle network. To minimize the fresh feedstock usage and maximize the recycled streams, it is necessary to segregate and reallocate the source streams to let them flow into corresponding sinks efficiently. Each source stream could be split in an optimal proportion, and then distributed to sinks. A graphical scheme is used to illustrate as shown in the Figure 4 below:

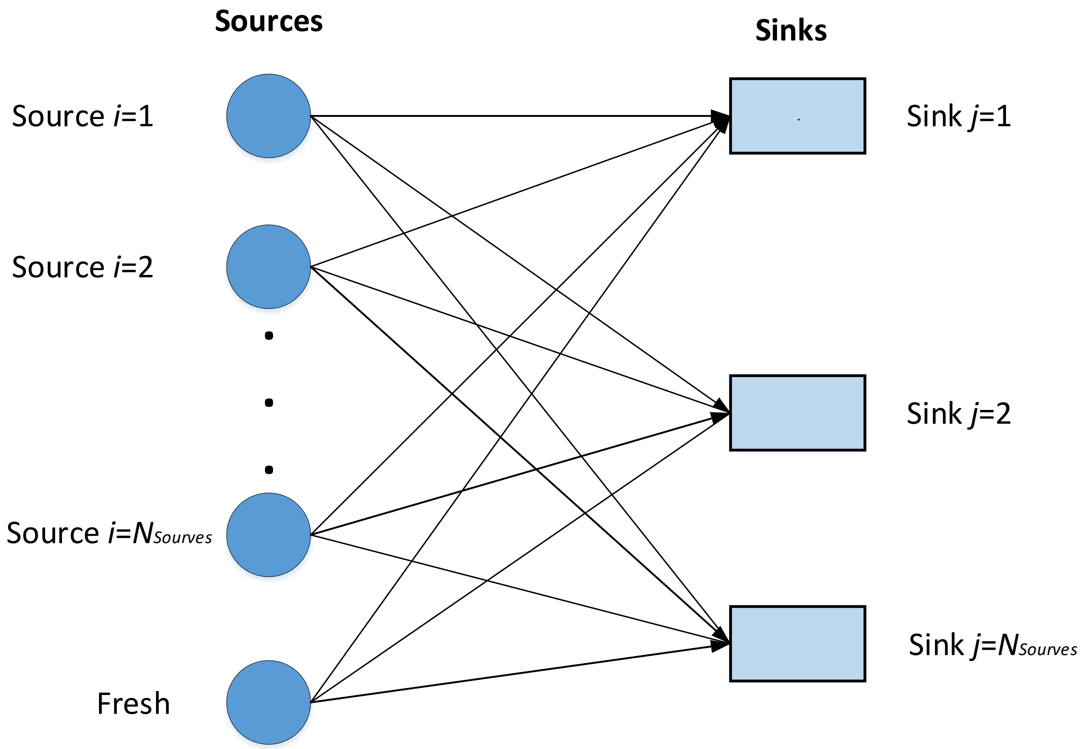


Figure 4. Schematic representation of the direct-recycle network for matching sources and sinks. (Adapted from [22])

After targeting, the first step of building a direct-recycle network is to rank sinks and source streams in ascending order based on their permissible composition of impurities. Set the sinks maximum load of impurities in ascending order one by one on the vertical axis, place the corresponding flow rate in the horizontal axis, then the sink composite curve is obtained, as shown in Figure 5. Similarly, the source composite curve could be obtained through the same method, as shown in Figure 6. These composite curves are accumulative representations of all process streams that treated for the building of recycle networks. Then the source composite curve and sink composite curve are on the same diagram, source composite curve is moved horizontally until it touches the sink composite curve, as shown in Figure 7. It is worth noting that once the source composite curve touches the sink composite curve, the horizontal movement should be stopped, overlap is not allowed in this method. The point where these two composite curves touch is the pinch point of the material recycle network.

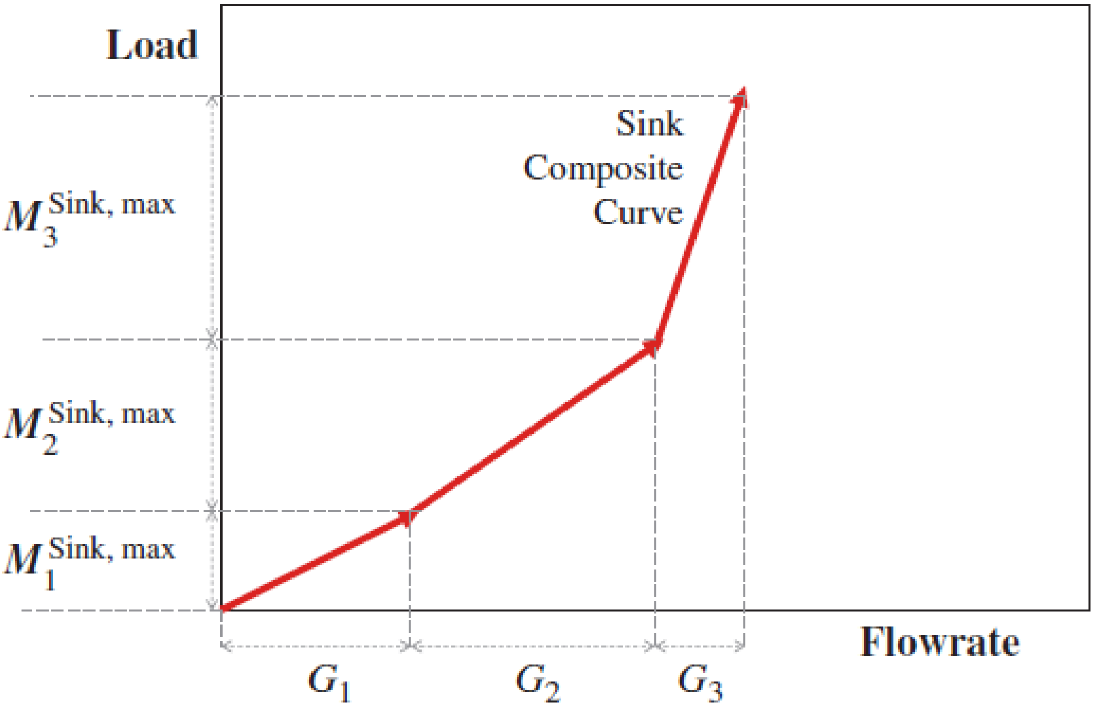


Figure 5. Developing the sink composite curve. (Adapted from [38])

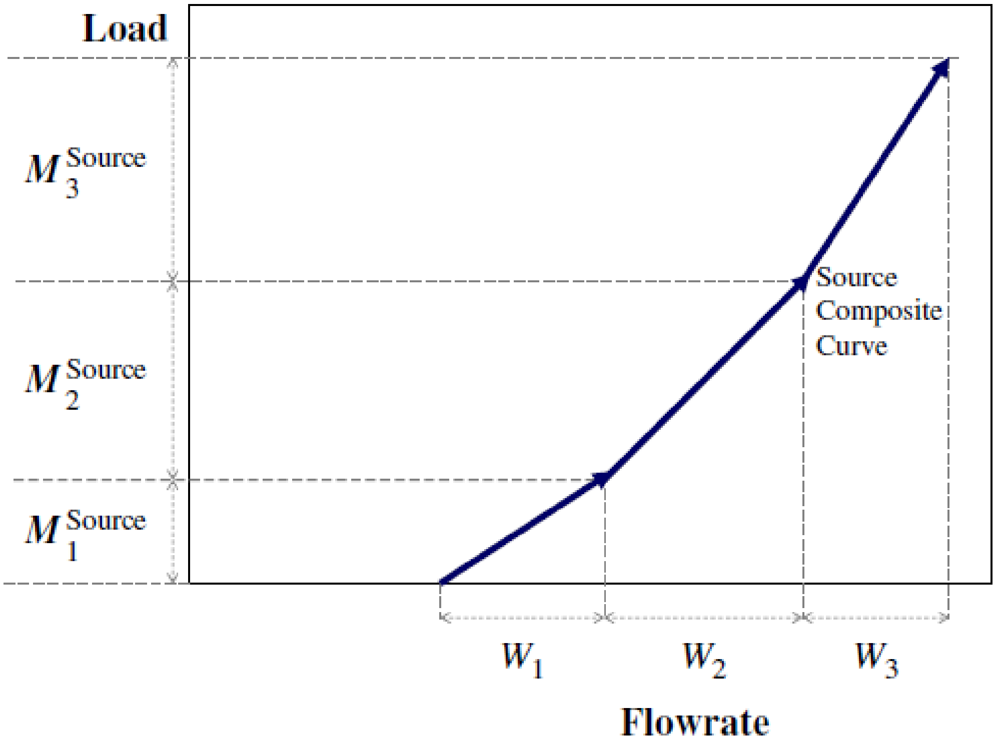


Figure 6. Developing the source composite curve. (Adapted from [38])

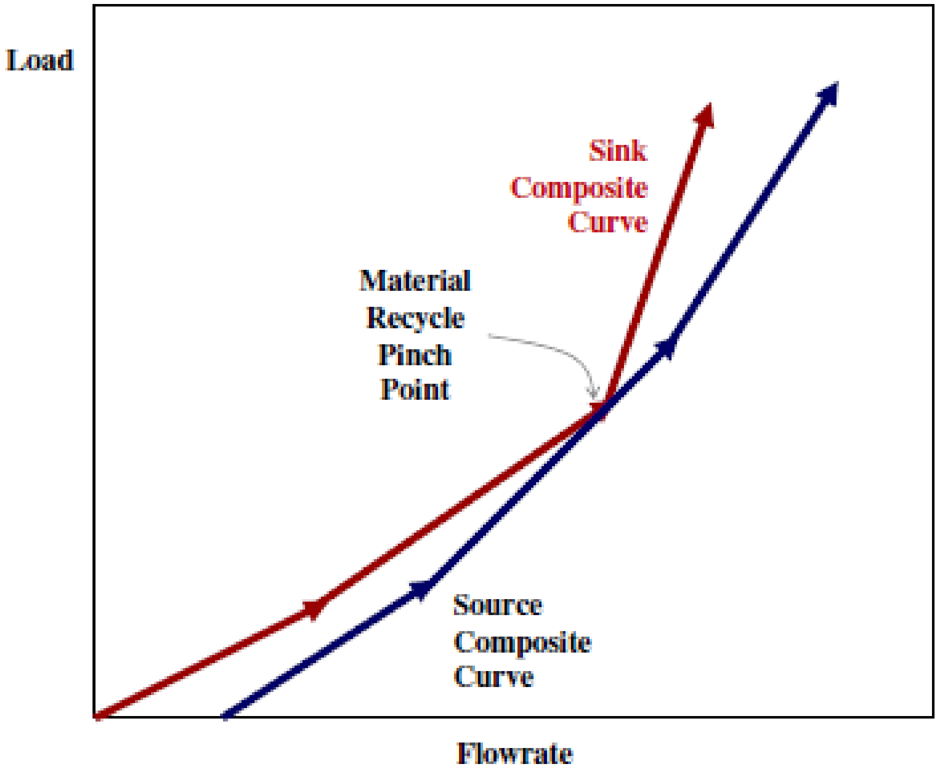


Figure 7. The material recycle pinch diagram. (Adapted from [38])

According to the material recycle pinch diagram, we can identify the targets of the recycle network as shown in Figure 9. The flowrate of sinks below the pinch point where there are no sources is the required minimum fresh usage. While the flowrate of sinks overlap with source composite curve is the maximum portion that could be directly recycled. The flowrate of sources above the pinch point where no matched sinks is the minimum waste discharge portion.

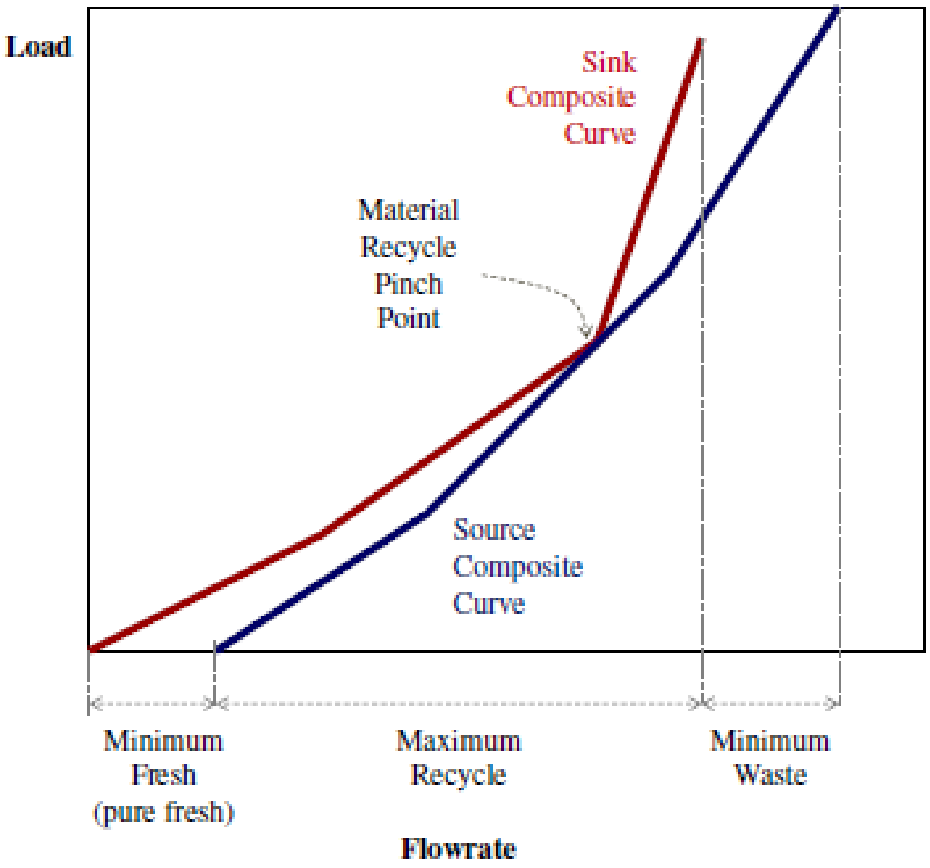


Figure 8. Identification of minimum fresh usage, maximum direct recycle and minimum waste discharge in the material recycle pinch diagram. (Adapted from [38])

Graphical approach is a useful and straightforward method. Under some scenarios, it is not easy to conduct. For example, when the amounts of sources and sinks are large, or there are some scaling problems, it will be very complicated to build the material recycle pinch diagram. To overcome these difficulties, an algebraic approach could be utilized to solve the direct-recycle network problems. With the help of an interval cascade diagram as shown in Figure 9, after input of process streams and calculation for sinks and sources in each interval, the most negative residue represents the minimum fresh usage of the whole network.

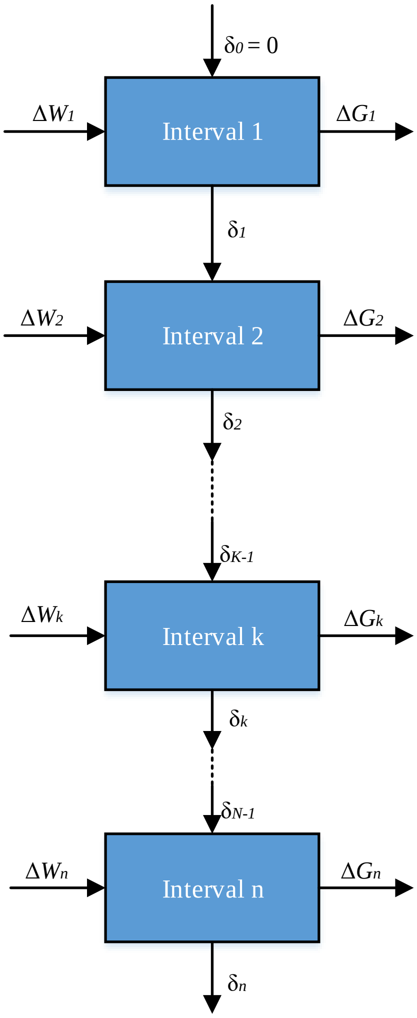


Figure 9. Cascade diagram. (Adapted from [52])

According to the cascade diagram of the existing system, we need to propose the material rerouting strategy for optimization. Based on the mass balance and capacities of each interval, a revised cascade diagram could be built to minimize the fresh usage and recover the load system, as shown in the figure below.

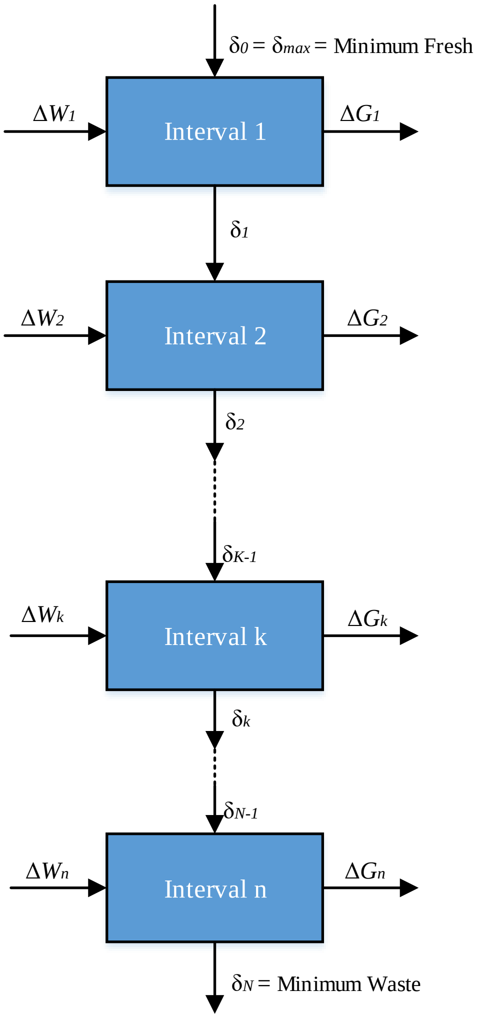


Figure 10. Revised cascade diagram. (Adapted from [52])

4.4 Economic, Sustainability and Safety Assessment

Chemical industry plays an important role in dominating and guiding the local economy. However, a series of problems appeared because of the contradictions among the local economy, social development and ecological environment, which have hindered the sustainability of the chemical industry. Therefore, quantitative assessments on economic, environmental sustainability and safety have been popular research topics for a long time. In the past a few decades, several metrics have been developed to assess economic viability, environmental sustainability, and safety, according to reviews of Roy et al.[53] and Hassim[54]. In addition, some multi-objective approaches which incorporating safety and/or sustainability analysis have been proposed.[55-58]

The economic return on investment (ROI) is a commonly used metric for assessing the cost-effectiveness of a project p, which could be expressed as below:

$$ROI_p = \frac{AEP_p}{TCI_p}$$

where AEP_p is the annual net economic profit for project p and TCI_p is the total capital investment of project p. In 2017, El-Halwagi introduced a new quantified metric referred as the sustainability weighted return on investment metric (SWROIM),[59] which incorporates different sustainability metrics into the return of investment, it could be expressed as below:

$$SWROIM_p = \frac{ASP_p}{TCI_p}$$

A new term referred as ASP_p , the annual sustainability weighted profit for project p, is also proposed, and it is defined as below:

$$ASP_p = AEP_p \left[1 + \sum_{i=1}^{N} wi \left(\frac{Indicator_{p,i}}{Indicator_i^{Target}}\right)\right]$$

where N is the number of indicators of different sustainability metrics, i is an index for the different indicators. The weighing factor wi is a ratio representing the relative importance of the ith indicator compared to the annual net profit. The term $Indicator_{p,i}$ represents the value of ith indicator associated with the pth project and the term $Indicator_i^{Target}$ represents the target value of the ith indicator. Therefore, the SWROIM of project p is defined as:

$$SWROIM_p = \frac{AEP_p \left[1 + \sum_{i=1}^{N} wi \left(\frac{Indicator_{p,i}}{Indicator_i^{Target}}\right)\right]}{TCI_p}$$

The SWROIM metric incorporates quantified sustainability assessment into economic analysis of a specific design, however, the other significant design objective, safety, is not included in this metric. In order to incorporate safety objective into the metric, a new term called Annual Safety and Sustainability Profit (ASSP) is proposed by El-Halwagi.[60] ASSP of a project p is defined as below:

$$ASSP_p = AEP_p \left[1 + \sum_{i=1}^{N} wi \left(\frac{Indicator_{base,i} - Indicator_{p,i}}{Indicator_{base,i} - Indicator_i^{Target}}\right)\right]$$

The $Indicator_{base,i} - Indicator_i^{Target}$ is the desired improvement associated with the project p. While the $Indicator_{base,i} - Indicator_{p,i}$ represents the actual improvement or deterioration of the project p. Therefore the ratio $\frac{Indicator_{base,i} - Indicator_{p,i}}{Indicator_{base,i} - Indicator_i^{Target}}$ represents the degree of actual improvement of project p meeting the desired objective. Then a new metric, the Safety and Sustainability Weighted Return on Investment (SASWROIM), is developed as shown below:[60]

$$SASWROIM_p = \frac{ASSP_p}{TCI_p}$$

$$= \frac{AEP_p \left[1 + \sum_{i=1}^{N} wi \left(\frac{Indicator_{base,i} - Indicator_{p,i}}{Indicator_{base,i} - Indicator_i^{Target}} \right) \right]}{TCI_p}$$

SASWORIM served as a comprehensive quantified metric that could be used for assessment from all the desired perspectives: economic viability, safety and environmental sustainability.

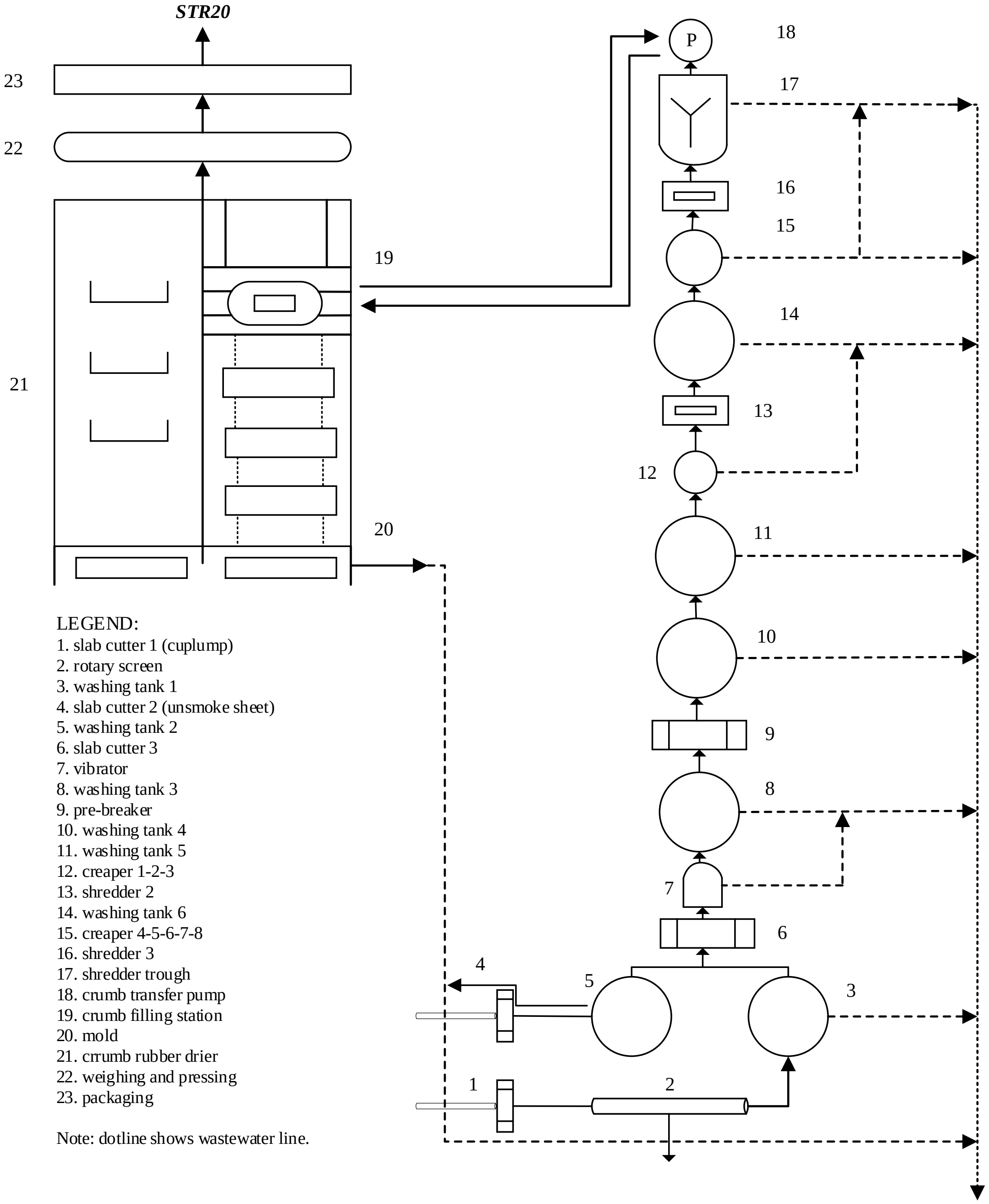
CHAPTER V

RESULTS AND DISCUSSION

5.1 Description of Case Study

Thailand is one of the largest exporters of natural rubber in the world. The processing of natural rubber consumes a large amount of fresh groundwater and discharges considerable quantities of wastewater. The overuse of water in the rubber and palm oil industries in Thailand has caused lots of problems, including contractions of the clay beds, aquifers drying up, and saltwater intrusion into fresh water aquifers in coastal areas. In addition, the over discharge of wastewater caused severe problem. For example, the wastewater that contained acidic compounds coupled with rubber particles resulted in eutrophication. Water body eutrophication caused oxygen depletion, which is a serious health risk for people living downstream.

A water reutilization facility in the rubber factory at Palian, Trang, Thailand was investigated as the case study. The detailed water reutilization process is described in the figure below.[61]



LEGEND:
1. slab cutter 1 (cuplump)
2. rotary screen
3. washing tank 1
4. slab cutter 2 (unsmoke sheet)
5. washing tank 2
6. slab cutter 3
7. vibrator
8. washing tank 3
9. pre-breaker
10. washing tank 4
11. washing tank 5
12. creaper 1-2-3
13. shredder 2
14. washing tank 6
15. creaper 4-5-6-7-8
16. shredder 3
17. shredder trough
18. crumb transfer pump
19. crumb filling station
20. mold
21. crrumb rubber drier
22. weighing and pressing
23. packaging

Note: dotline shows wastewater line.

Figure 11. Wastewater streams in STR20 production plant. (Adapted from [61])

The total land area for the wastewater treatment system is 21668 m^2. The operational capacity of the factory is 40 ton/day of high grade Stand Thai Rubber (STR20).[61] A mixture of cup lump and unsmoked sheet rubber is the raw material. Main processes in this facility include washing, grinding, drying and compaction. Initially, cup lump rubber is transferred into a slab cutter (1) followed by a rotary screen (2). Impurities are removed through washing tank 1 (3). Then the washed cup lump rubber is mixed with washed unsmoked sheet rubber from washing tank 2 (5). After being processed in another slab cutter (6) and a vibrator (7), further washing units, washing tank 3 (8), washing tank 4 (10) and washing tank 5 (11), are utilized for the secondary cleaning. The creeper 1-2-3-4-5-6-7-8 (15) and shredder 2 (16) are used to transform the raw rubber material into the proper shape. Shredded rubber is transferred into mold blocks (20). Flue gas from the drier is scrubbed through a wet scrubber. Finally, rubber is weighted and compacted and then packed for export. Wastewater from both the mold blocks and the cleaning units are discharged to the drainage system. The flowsheet of water with flow rates is described in the following figure, which also includes domestic and service water use.

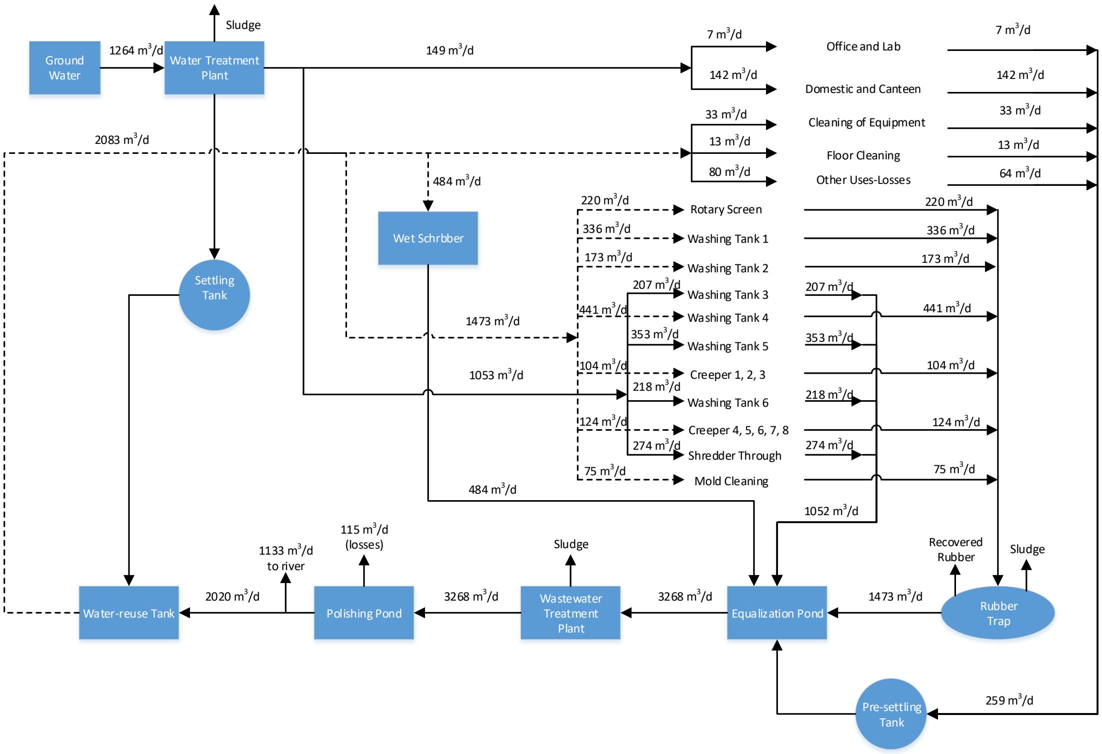


Figure 12. Water balance of the rubber factory with existing water usage. (Adapted from [61])

The bottom part in Figure 12 shows a brief description of the existing water treatment system. The flow rate of ground water and recycled water is all based on this existing treatment facility. This water treatment system costs $168,302 annually with raw water consumption and water discharge to the river at 1264 $\frac{m^3}{d}$ and 1133$\frac{m^3}{d}$, respectively.

5.2 Objective of the Case Study

This case study focused on selection of water treatment technology that satisfies the requirements on discharged water. Utilization of mass integration of possible water streams can reduce fresh water usage to achieve the goals of improvement of safety performance, economic viability and environmental sustainability.

Sustainability enhancement of this rubber plant was achieved through reducing fresh water usage. Safety enhancement of this process was achieved through reducing wastewater discharge.

5.3. Analysis of Process Streams and Segregation

Table 1 [61] provides characteristics of the wastewater streams in this facility. All the streams are divided into four groups: domestic wastewater, low strength process wastewater, wet scrubber wastewater and high strength process wastewater. Low strength process wastewater includes water from the following units: washing tank 3, washing tank 5, washing tank 6, the shredder trough. High strength process wastewater mainly comes from the rotary screen, washing tank 1, washing tank 2, washing tank 4, creepers1-8, and the molds.

Table 1. Rubber wastewater characteristics at different processing units. (Adapted from [61])

Parameter	**Rotary Screen**	**Washing Tank 1**	**Washing Tank 2**	**Washing Tank 3**	**Washing Tank 4**	**Washing Tank 5**	**Creeper 1, 2, 3**	**Washing Tank 6**	**Creeper 4, 5, 6, 7, 8**	**Shredder**	**Molding**	**Wet Scrubber**	**Combined Wastewater**
Temperature (°C)	28	29	28	30	29	29	29	30	30	29	28	65	30
pH	7.8	7.6	7.2	7.7	7.7	7.4	7.9	7.1	7.8	7.9	7.5	7.8	7.5
BOD (mg/L)	482	161	255	141	168	109	123	111	142	100	192	193	225
COD (mg/L)	2089	299	558	219	338	129	372	192	227	261	264	335	552
Total Solid (mg/L)	4380	3047	2159	4628	4503	2452	4338	2901	3297	5280	4528	2758	6761
S. Solid (mg/L)	2445	224	235	125	235	122	213	123	192	117	167	125	301
Total Nitrogen (mg/L)	130	74	83	67	60	58	57	36	60	51	68	70	68
NH$_3$-Nitrogen (mg/L)	82	49	55	40	43	30	41	20	43	49	48	52	51
Total Phosphorus (mg/L)	25	17	22	16	17	13	17	12	17	18	18	14	16
Sulfate (mg/L)	7	6.9	6.5	6.7	8.1	4.8	7.7	5	7.5	7.8	7.4	7.6	6.6

The criteria for such stream segregation is based on the amount of suspended solids in the wastewater. BOD is the key criteria used in industry, therefore BOD value was used for calculations as well.

5.4. Identification of Possible Sources and Sinks

Based on previous analysis and data in Table 1, process streams were divided into several groups as shown in Tables 2, 3 and 4 (known as sources in integration terms). Sources are divided into three levels: low strength process wastewater, high strength process wastewater and wet scrubber wastewater. Flow rate, impurity concentration and load are obtained from the description of the existing system. Data for domestic wastewater are obtained from the public water treatment department.

Table 2. Source data for low strength process wastewater.

No.	Description (wastewater from)	Flow (m^3/d)	Impurity Concentration (mg/l)	Load (g/day)
1	Washing Tank 3	259	141	29187
2	Washing Tank 5	353	109	38477
3	Washing Tank 6	218	111	24198
4	Shredder Trough	274	100	27400
Sum	low strength process wastewater	1052	113.4	119262

Table 3. Source data for high strength process wastewater.

No.	**Description (wastewater from)**	**Flow (m^3/d)**	**Impurity Concentration (mg/l)**	**Load (g/day)**
1	Rotary Screen	220	482	106040
2	Washing Tank 1	336	161	54096
3	Washing Tank 2	173	255	44115
4	Washing Tank 4	441	168	74088
5	Creeper 1,2,3	104	123	12792
6	Creeper 4,5,6,7,8	124	142	17608
7	Molding	75	192	14400
Sum	high strength process wastewater	1473	219.4	323139

Table 4. Source data for wet scrubber wastewater.

	Description (wastewater from)	**Flow (m3/d)**	**Impurity Concentration (mg/l)**	**Load (g/day)**
Sum	Wet scrubber	484	193	93412

Water consuming units (known as sinks in integration terms) are divided into three groups based on the degree of cleanness of the water: super clean, clean, and acceptable clean. Tables 5, 6, 7 show the detailed data for sinks. Flow rate and load are obtained from the description of the existing system. Maximum inlet impurity fractions are assumed based on research of various current standards.

Table 5. Sink data for super clean water needed.

No.	Description (water for)	Flow (m^3/d)	Max Inlet Impurity Fraction (mg/l)	Load (g/day)
1	Office and lab	7	5	35
2	Domestic and canteen	142	10	1420
Stream	Super clean water supply	149	5	745

Table 6. Sink data for clean water needed.

No.	Description (water for)	Flow (m^3/d)	Max Inlet Impurity Fraction (mg/l)	Load (g/day)
1	Cleaning of equipment	33	20	660
2	Floor cleaning	13	20	260
3	Other use	80	35	2800
4	Washing tank 3	207	10	2070
5	Washing tank 5	353	10	3530
6	Washing tank 6	218	10	2180
7	Shredder Trough	274	15	4110
Stream	Clean water supply	1178	10	11780

Table 7. Sink data for acceptable clean water needed.

No.	Description (water for)	Flow (m^3/d)	Max Inlet Impurity Fraction (mg/l)	Load (g/day)
1	Rotary Screen	220	18	3960
2	Washing Tank 1	336	20	6720
3	Washing Tank 2	173	20	3460
4	Washing Tank 4	441	20	8820
5	Creeper 1,2,3	104	62.5	6500
6	Creeper 4,5,6,7,8	124	40	4960
7	Molding	75	100	7500
8	Wet scrubber	484	50	24200
Stream	Acceptable clean water supply	1957	18	35226

5.5 Selection of Proper Water Treatment Methods

Due to different water usage requirements, wastewater should be treated before reuse by sinks instead of by direct cycle.

Utilization of artificial natural processes is one way to treat wastewater. A constructed wetland, such as an artificial marsh or swamp that includes substrate, vegetation and biological organisms, is a good wastewater treatment system. This kind of system could remove nutrients, suspended solids and organic compounds with low cost and high efficiency. However, this method has a high land spacing requirement.[62-64]

Chemical agents, such as hypochlorous acid, could serve as oxidizing agents for organic destruction of the rubber wastewater.[65] The results showed efficiencies of 99.9% and 98.8% for COD and BOD removal, respectively. However, the disadvantages of this method cannot be ignored: cost is varied and sensitive due to the price fluctuation of the specific chemical agent. Therefore, this method is not a robust and cost-stable way to process wastewater, and is not suitable for long-term operation and production.

The biological method has some unique advantages compared with other approaches; due to its flexibility, it can incorporate with other techniques. For example, when incorporated with sulphate reduction system, it is a low-cost operation with high removal efficiency. In addition, biogas could be produced during the treatment as an energy source.[66] The biological method can incorporate with precipitation, which could lower concentrations of heavy metals, such as zinc, in wastewater.[67, 68]

Membrane distillation is established as one kind of wastewater reverse osmosis concentrate (WWROC). Reverse osmosis is a water treatment technology which uses semipermeable membrane to remove large molecules as well as ions. A proper pressure would be used to overcome osmotic pressure, driven by differences between the solvents and chemical concentrations. Therefore, WWROC is a great approach for BOD treatment.

There are a lot of other technologies widely utilized for the wastewater treatment currently, such as anaerobic filter, up-flow anaerobic sludge blanket (UASB), electrochemical methods, gas injection technique and so on.[62] This study implemented wastewater treatment processes to the existing facility to improve the sustainability of the whole system.

5.6 Synthesis of Mass-Exchange Network

Due to the high concentrations of contaminants of wastewater streams, they cannot be recycled directly. Mass exchange networks (MENs) were synthesized to reduce the concentrations of impurities. The following table provides a summary of data for segregated streams (known as rich streams in integration terms). The fourth column transfers volume flow rate into mass flow rate. Density of water is assumed as 1000kg/m^3.

Since there are no process lean streams, external mass separation agents were required. Three external MSAs were considered as candidates: activated carbon (S1), reverse osmosis (S2) and gas injection (S3). The data for the candidate MSAs are given in Table 9. The equilibrium data for the transfer of the pollutant from the waste stream to the jth MSA is given by

$$y_j = m_j(x_j + \varepsilon_j) + b_j$$

where y_j and x_j are the mass fractions of the organic pollutant in the wastewater and the jth MSA, respectively.

Table 8. Rich streams data.

Stream	**Description**	**Flow (m^3/d)**	**Flow (kg/s)**	**Supply composition y_s (ppmw)**	**Target composition y_t (ppmw)**	**Exchanged mass (mg/s)**
R1	Domestic wastewater	259	3	150	15	405
R2	High strength process wastewater	1473	17	219.4	30	3219.8
R3	Low strength process wastewater	1052	12	113.4	15	1180.8
R4	Wet scrubber wastewater	484	5.6	193	20	968.8

Table 9. Lean streams data.

Stream	**Upper bound on flow rate L_j (kg/s)**	**Supply composition x_s (ppmw)**	**Target composition x_t (ppmw)**	m_j	ε_j **(ppmw)**	c_j **฿/kg**
S1	∞	300	1000	1.0	100	0.001
S2	∞	10	200	0.8	50	0.005
S3	∞	20	600	0.2	50	0.01

According to the pinch diagram shown in Figure 13, the minimum operating cost of the MEN was obtained. The following pinch diagram is synthesized.

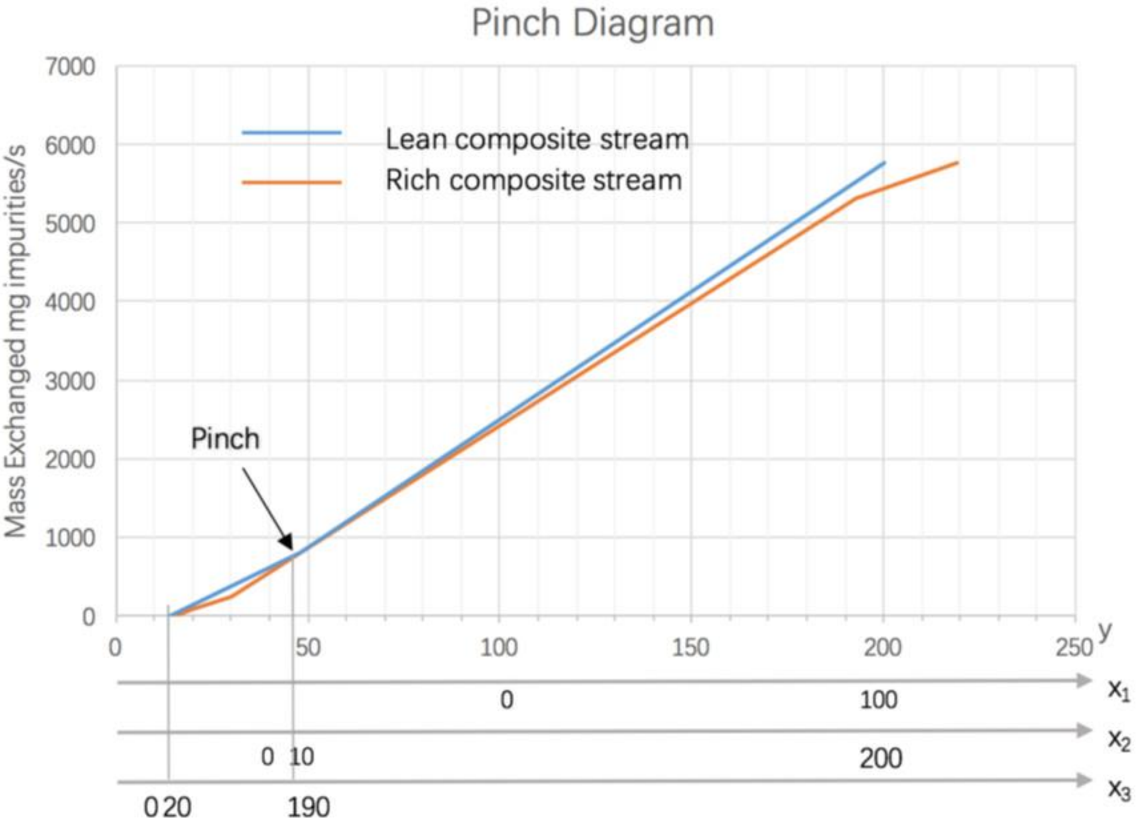


Figure 13. The mass exchange pinch diagram.

As shown from pinch diagram above, S2 and S3 were selected as the MSAs. The flow rates are 26.18kg/s and 4.71kg/s which are the slopes of blue line. Cost of MSAs is 143539 $/yr.

5.7 Synthesis of Direct Recycle Network

After the Mass Exchange Networks processing, wastewater reached the requirements of water usage and became available for recycle. The next phase is the design of direct mass recycle networks to integrate and optimize the water supply system, lower the usage of fresh water and cost. Table 10 and 11 are the summary of sources and sinks for this recycle network.

Table 10. Source streams data for water recycle network.

Streams	Flow rate (kg/s)	Mass frac of impurities (ppmw)	Load of impurities (mg/s)
R1	3	15	45
R2	17	30	510
R3	12	15	180
R4	5.6	20	112

Table 11. Sink data for water recycle network.

Sink	Flow rate (m^3/d)	Flow rate (kg/s)	Max inlet mass frac of impurities (ppmw)	Max inlet load of impurities (mg/s)
Sink using acceptable clean water (**Sink 1**)	1957	22.7	18	408.6
Sink using clean water (**Sink 2**)	1178	13.7	10	137
Sink using super clean water (**Sink 3**)	149	1.7	5	8.5

Segregation, mixing, and recycle were utilized to synthesize the recycle network, identify a target for minimum water usage and minimum waste discharge. Two different methods, graphic and algebraic approach, were used for calculation in this part.

Based on the calculations in Table 10, Table 11, the algebraic procedure for direct-recycle network can be summarized in Table 12 as follows.

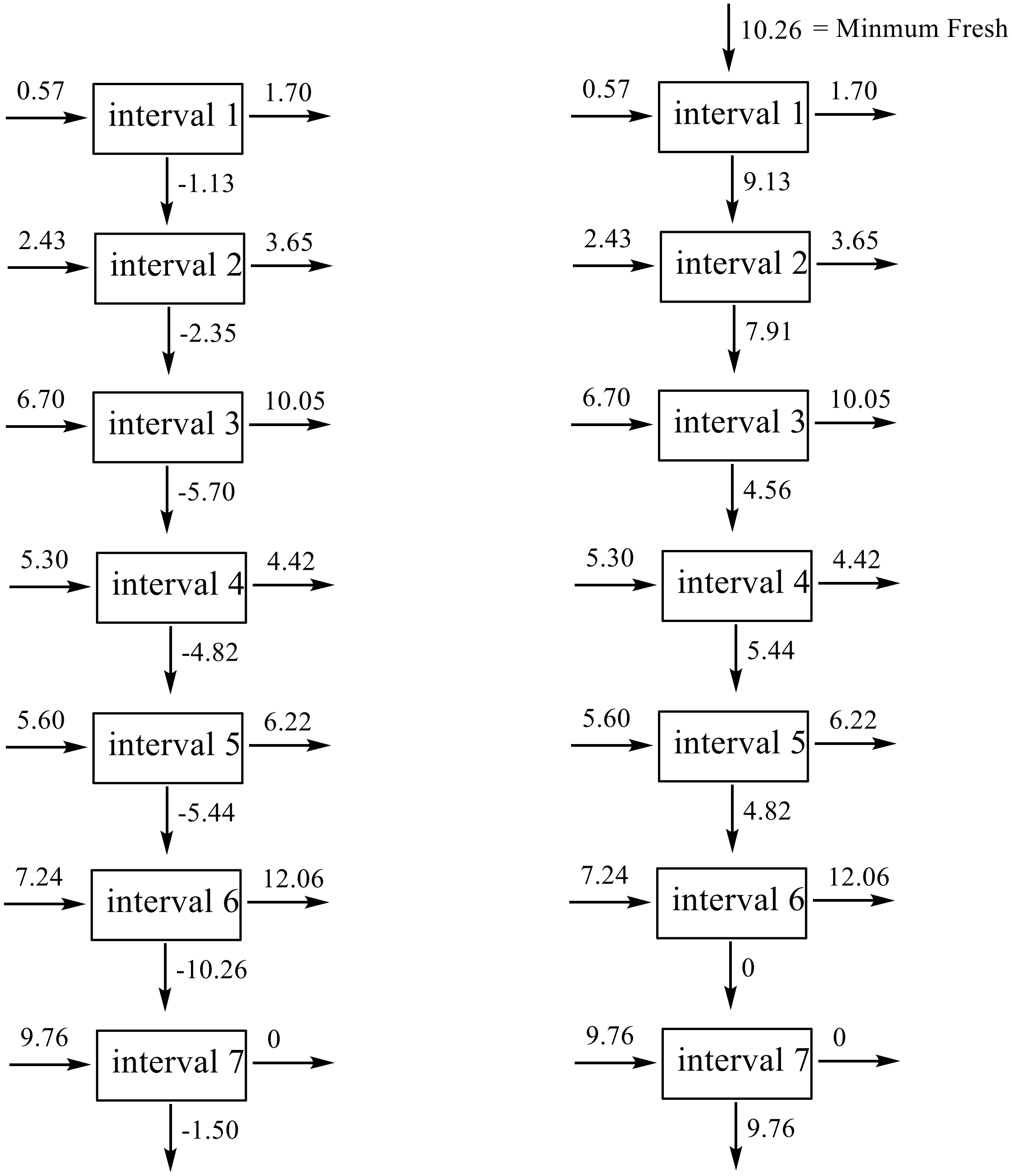
Table 12. Load-interval Diagram.

Interval	Load (kg/s)	Interval Load (kg/s)	Source	Source Flow per Interval (kg/s)	Sink	Sink Flow per Interval (kg/s)
1	8.5	8.5	Source 1	0.57	Sink 3	1.70
2	45	36.5		2.43	Sink2	3.65
3	145.5	100.5	Source 3	6.70		10.05
4	225	79.5		5.30	Sink 1	4.42
5	337	112	Source 4	5.60		6.22
6	554.1	217.1	Source 2	7.24		12.06
7	847	292.9		9.76		

The original cascade diagram for the existing water utilization network was constructed in the Figure 14 (left), based on Table 5.12. According to the original cascade diagram, it is obvious that minimum fresh water usage was 10.29 kg/s. A revised cascade diagram was proposed and shown on the right of Figure 14. Pinch point is located between interval 6 and 7.

Graphical pinch diagram was also conducted as shown in Figure 15. According to the graphical pinch diagram, the minimum fresh water usage and minimum waste discharge is 10.29 kg/s and 9.76 kg/s, respectively. These results matched algebraic conclusions as well.

Based on algebraic and graphical methods, a detailed implementation was proposed as shown in Figure 16 to illuminate how water should distribute from sources to sinks.



Cascade Diagram **Revised Cascade Diagram**

Figure 14. Load-interval cascade diagram.

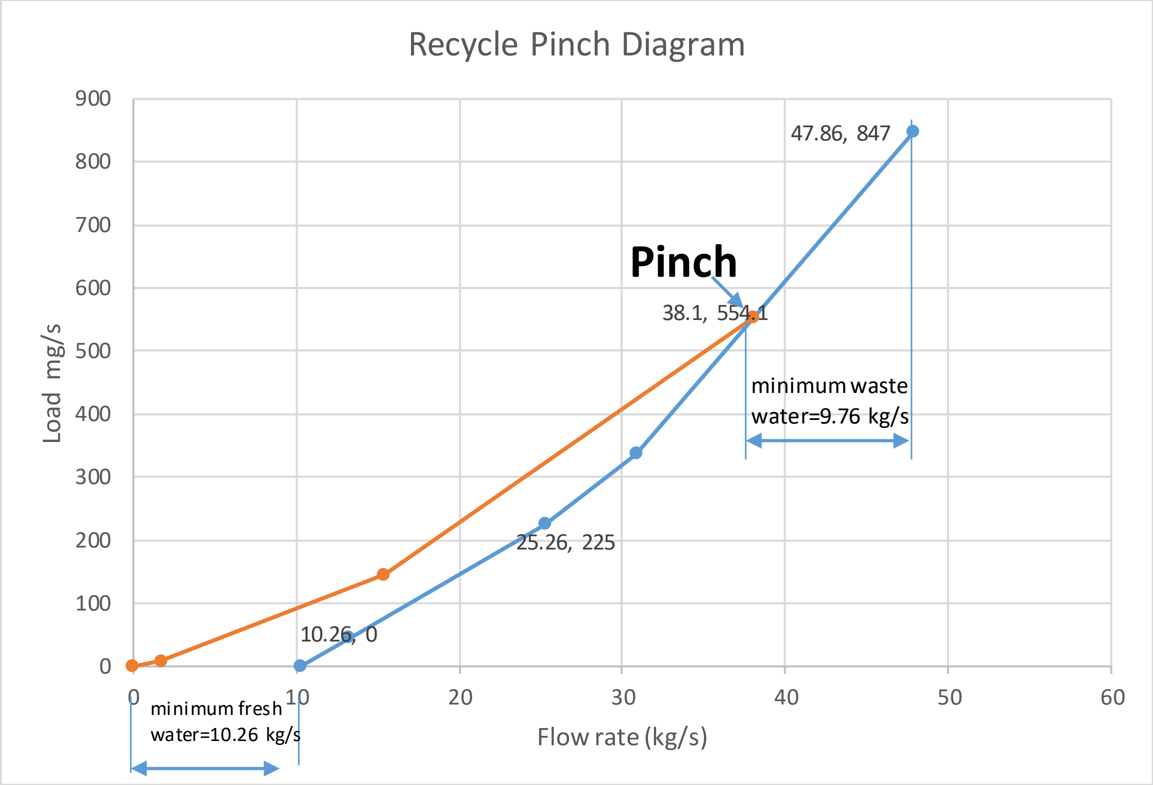


Figure 15. Recycle pinch diagram.

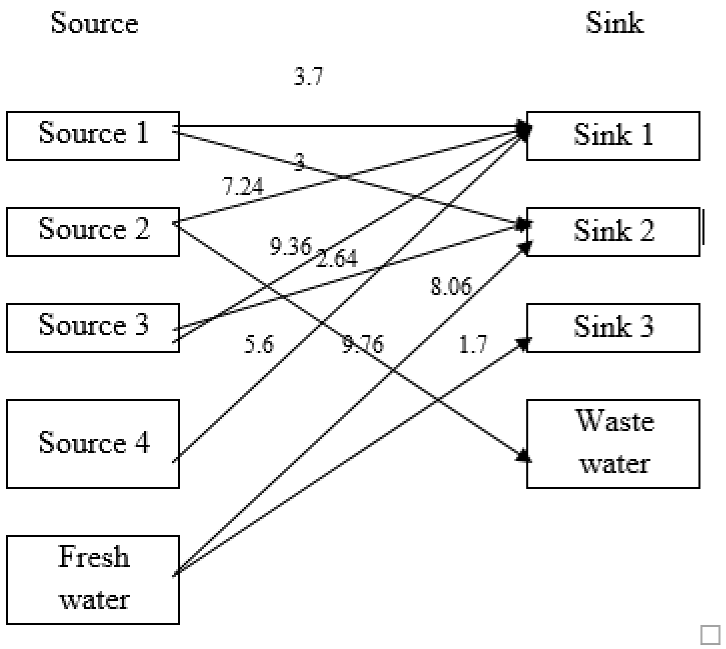


Figure 16. Proposed implementation.

5.8 Safety, Environmental Sustainability and Economic Viability Analysis

Hierarchy of hazards control is an effective loss prevention system that is widely accepted by a variety of industries.[69] It's a very feasible and practical management approach in workplace, a lot of process industry facilities have developed this approach as a widespread practice for loss prevention. The hierarchy of hazards control is illustrated as shown below:

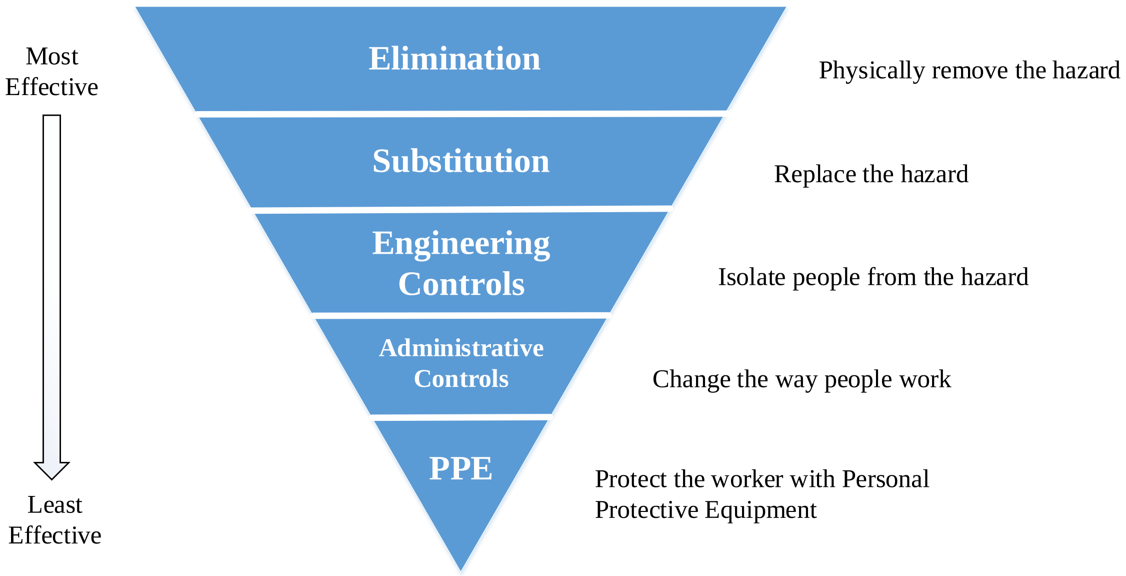


Figure 17. Hierarchy of hazard controls.

As shown in the graphic illustration, elimination and substitution are the two most effective methods that can remove hazards from the root cause. While many hazardous materials are required and irreplaceable in various processes, these two methods are not accessible in a lot of scenarios. In this case study, the hazardous wastewater was eliminated to a certain extent through reducing the wastewater discharge. A comparison between optimized water reuse system and existing water reuse system was conducted in terms of annual fresh water consumption, wastewater discharge and water treatment cost results are shown in Table 13.

Table 13. Comparison with existing water treatments

Parameter	Existing Water Reuse System	Optimized Water Reuse System
Fresh water consumption(ton/year)	461×10^3	323×10^3
Wastewater discharged (ton/year)	413×10^3	307×10^3
Annual water treatment cost ($)	168×10^3	143×10^3

Based on the data of Table 13, after the optimization of the wastewater reuse system, the annual water treatment cost is reduced from $\$168 \times 10^3$ to $\$143 \times 10^3$. Fresh water consumption and wastewater discharge is reduced by 30% and 26%, respectively.

In this case study, the Sustainability Weighted Return on Investment ($SWROIM$) is utilized as the quantitative assessment for optimized water reuse system. The $SWROIM$ of a project p could be calculated as shown below:

$$SWROIM_p = \frac{ASP_p}{TCI_p}$$

The AEP is assumed not change, so the incremental $SWROIM$, $\Delta SWROIM_p$, is defined as shown below:

$$\Delta SWROIM_p = \frac{\Delta ASP_p}{TCI_p}$$

$$= \frac{AEP_p \left[1 + \sum_{i=1}^{N} wi \left(\frac{Indicator_{existing,i} - Indicator_{p,i}}{Indicator_{existing,i} - Indicator_i^{Target}} \right) \right]}{TCI_p}$$

The annual water treatment cost can be assumed as the total capital investment (*TCI*) in this case study. The annual net economic profit (*AEP*) is assumed as a constant. According to the expression above, if other conditions are constant, the value of $SWROIM$ is proportional to the values of weighing factors. In this case study, the weighting factor of fresh water usage, w_{fresh}, is assumed as 0.10. The weighting factor of wastewater discharge, w_{waste}, is assumed as 0.15. $Indicator_{existing,fresh} - Indicator_{fresh}^{Target}$ represents the maximum desired reduction of fresh water, which is assumed as 60% of the fresh water usage of the existing system:

$$Indicator_{existing,fresh} - Indicator_{fresh}^{Target} = 461 \times 10^3 \frac{ton}{year} \times 60\%$$

$$= 276 \times 10^3 \frac{ton}{year}$$

$Indicator_{existing,fresh} - Indicator_{fresh}$ represents the actual reduction of fresh water, which is calculated as shown below:

$$Indicator_{existing,fresh} - Indicator_{fresh}^{Target} = 461 \times 10^3\ ton/year - 323 \times 10^3\,\frac{\text{ton}}{\text{year}}$$

$$= 138 \times 10^3\,\frac{ton}{year}$$

Similarly, $Indicator_{existing,fresh} - Indicator_{waste}^{Target}$ represents the maximum desired reduction of wastewater discharge, which is assumed as 50% of the wastewater discharge of the existing system:

$$Indicator_{existing,fresh} - Indicator_{waste}^{Target} = 413 \times 10^3\,\frac{ton}{year} \times 50\%$$

$$= 206 \times 10^3\,\frac{ton}{year}$$

$Indicator_{existing,fresh} - Indicator_{fresh}$ represents the actual reduction of fresh water, which is calculated as shown below:

$$Indicator_{existing,fresh} - Indicator_{waste}^{Target} = 413 \times 10^3\,\frac{ton}{year} - 307 \times 10^3\,\frac{ton}{year}$$

$$= 106 \times 10^3\,\frac{ton}{year}$$

The $\Delta SWROIM$ of the optimized new wastewater reuse system compared with the existing water reuse system can be calculated as shown below:

$$\Delta SWROIM_{optimized} = \frac{ASP_{optimized}}{TCI_{optimized}}$$

$$= \frac{AEP \quad \left[1 + \sum_{i=1}^{2} wi\left(\frac{Indicator_{existing,i} - Indicator_{p,i}}{Indicator_{existing,i} - Indicator_{i}^{Target}}\right)\right]}{TCI_{optimized}}$$

$$= \frac{AEP \quad \left[1 + 0.10 \times \frac{140{,}813\,\frac{ton}{year}}{276{,}823\,\frac{ton}{year}} + 0.15 \times \frac{105{,}646\,\frac{ton}{year}}{206{,}719\,\frac{ton}{year}}\right]}{\$143{,}539}$$

$$= \frac{1.13AEP}{TCI_{optimized}}$$

$$SWROIM_{oexisting} = \frac{AEP}{TCI_{existing}}$$

Compared to the existing wastewater reuse network, the increasing rate of $SWROIM$ of proposed optimal wastewater reuse network can be expressed as below:

$$Increasing\ Rate\ of\ SWROIM \quad = \frac{\Delta SWROIM_{optimized}}{SWROIM_{oexisting}} = \ 32\%$$

In this scenario where w_{fresh} and w_{waste} is assumed as 0.10 and 0.15, respectively, the increasing rate of $SWROIM$ is 32% compared to the existing wastewater reuse network. This noteworthy increment could be utilized as a quantified assessment in terms of safety, environmental sustainability and economic viability. As mentioned before, the $SWROIM$ is proportional to the value of weighting factors, which means if the decision-maker values safety and environmental sustainability than other factors, the increment will be more significant.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This work developed an optimized water reuse network model for hazardous wastewater via mass integration and pinch-analysis. The optimized model was synthesized based on the analysis of existing water network to improve the safety, environmental sustainability and economic viability of the water reuse system. The following tasks have been performed:

- Identifications of possible sources and sinks for wastewater reutilization
- Proper wastewater treatment technologies and MSAs were selected to meet the various requirements of sinks
- Mass integration and pinch-analysis were conducted for the optimal wastewater mass-exchange network
- Economic, environmental sustainability and safety metrics were utilized for assessment of the proposed model

A case study has been developed to assess hazardous wastewater reutilization network of an operational capacity of the factory is 40 ton/day of high grade Stand Thai Rubber (STR20). An optimal new wastewater reutilization network was proposed, some key enhancements on safety, environmental sustainability and economic viability are as shown below:

- Annual fresh water consumption was reduced from 461×10^3 tonnes to 323×10^3 tonnes
- Annual wastewater discharge was reduced from 413×10^3 tonnes to 307×10^3 tonnes
- Annual water treatment cost in this facility was reduced from $\$168 \times 10^3$ to $\$143 \times 10^3$

This study provides an optimized model for hazardous wastewater reutilization networks. However, implementation cost of the proposed design is necessary to consider under different scenarios. In addition, further study needs to be conducted to investigate the treatment methods for unrecycled hazardous wastewater.

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