

**PROCESS INTEGRATION TECHNIQUES FOR OPTIMIZING
SEAWATER COOLING SYSTEMS
AND BIOCIDES DISCHARGE**

A Thesis

by

ABDULLAH S. BINMAHFOUZ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

December 2005

Major Subject: Chemical Engineering

**PROCESS INTEGRATION TECHNIQUES FOR OPTIMIZING
SEAWATER COOLING SYSTEMS
AND BIOCIDES DISCHARGE**

A Thesis

by

ABDULLAH S. BINMAHFOUZ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Chair of Committee,
Committee Members,

Head of Department,

Mahmoud M. El-Halwagi
Mahboobul Mannan
Juergen Hahn
Bill Batchelor
Kenneth R. Hall

December 2005

Major Subject: Chemical Engineering

ABSTRACT

Process Integration Techniques for Optimizing Seawater Cooling Systems
and Biocide Discharge. (December 2005)

Abdullah S. BinMahfouz, B.S., King Fahd University of Petroleum & Minerals,
Dhahran, Saudi Arabia;

M.B.A., Indiana University of Pennsylvania

Chair of Advisory Committee: Dr. Mahmoud El-Halwagi

This work addresses the problem of using seawater for cooling and the associated environmental problems caused by the usage and discharge of biocides. The discharged biocide and its byproducts are toxic to aquatic lives and must be decreased below certain discharge limits on load prior to discharge. The conventional approach has been to add biocide removal units as an end-of-pipe treatment. This work introduces an integrated approach to reducing biocide discharge throughout a set of coordinated strategies for in-plant modifications and biocide removal. In particular, process integration tools are used to reduce heating and cooling requirements through the synthesis of a heat-exchange network. Heat integration among process of hot and cold streams is pursued to an economic extent by reconciling cost reduction in utilities versus any additional capital investment of the heat exchangers. Other strategies include maximization of the temperature range for seawater through the process and optimization of biocide dosage. This new approach has the advantage of providing cost savings while reducing the usage

and discharge of biocides. A case study is used to illustrate the usefulness of this new approach and the accompanying design techniques.

DEDICATION

I would like to devote my academic work to the spirit of my father who encouraged me to continue my education and helped me to set my essential goals in my life. I am deeply grateful to my mother who has always supported me in all stages of life and has continually encouraged me to pursue my educational objectives. Many thanks to my mother-in-law who has never stopped praying for my success in my studies and in my life. Special thanks are due to my wife who has always been there for me supporting and encouraging me with unconditional love to continue my education and to make my dreams come true. Also, much love to my daughters Mariam and Dhoha, the lights of my life. I would like to thank all my brothers and sisters and the rest of my family for their love and support.

ACKNOWLEDGEMENTS

I am very grateful and thankful to my God Allah for blessing me with ability and capability to gain the knowledge, and helping me throughout my life particularly in my studies.

There are many people who have helped me in my graduate studies and have encouraged me. At the top of them is my advisor Dr. Mahmoud El-Halwagi. I have been honored to work under Dr. El-Halwagi's supervision. He has provided me with guidance, encouragements, and advice during my coursework and research. I am personally indebted to Dr. El-Halwagi for all his concern and care.

I would like to thank my committee members Dr. Batchelor, Dr. Hahn, and Dr. Mannan, for serving on my thesis committee and for their very valuable input, support, and time.

I would like to thank my professors who taught me in Indiana University of Pennsylvania during my MBA studies and gave me encouragement to continue my education and join engineering graduate school. Special thanks are due to professor Krishnan, my academic advisor, for his kind advises and help. Appreciation is due to professor Al-Bohali who introduced me to the field of optimization which led me later on to process integration my research area in graduate studies in chemical engineering.

I would like to thank all my classmates for their time and help during my course work, and for helping me overcome the gap of more than ten years away from the engineering school. Also, I would like to thank my group mates specially Daniel, Tanya, and Qin and my officemates Abdul Aziz, Ben, Meteab, Musaed, and Nasser.

TABLE OF CONTENTS

		Page
ABSTRACT.....		iii
DEDICATION.....		v
ACKNOWLEDGEMENTS.....		vi
TABLE OF CONTENTS.....		viii
LIST OF FIGURES.....		x
LIST OF TABLES.....		xii
NOMENCLATURE.....		xiii
CHAPTER		
I	INTRODUCTION.....	1
II	LITERATURE REVIEW.....	6
	2.1. Biocide Dosage.....	6
	2.2. Basic Chemistry of Chlorine-Based Disinfection.....	7
	2.3. Bromide- and Bromine-Based Disinfection.....	9
	2.4. Disinfection Kinetics.....	11
III	PROBLEM STATEMENT.....	13
IV	THEORETICAL STUDY AND DESIGN APPROACH.....	16
	4.1. Rationale and Overview of Proposed Design Procedure.....	16
	4.2. Heat Integration Analysis.....	20
	4.3. Maximization of Temperature Span.....	36
	4.5. Dosage Optimization.....	38
	4.6. End-of-pipe Treatment.....	39

CHAPTER		Page
V	CASE STUDY AND DISCUSSION OF RESULTS.....	40
	5.1. Process Description.....	40
	5.2. Heat Integration.....	48
	5.3. Maximizing Discharged Temperature.....	64
	5.4. Minimizing Chlorine Dosage.....	65
VI	CONCLUSIONS AND RECOMMENDATIONS.....	72
	REFERENCES.....	74
	VITA.....	76

LIST OF FIGURES

	Page
Fig. 2.1 Chlorination-Species Distribution as a Function of pH (Based on Data by Oldfield & Todd 1981).....	8
Fig. 2.2 Bromination-species Distribution as a Function of pH (Based on Data by Oldfield & Todd 1981).....	11
Fig. 3.1 A Schematic Representation of the Stated Problem.....	14
Fig. 4.1 Design Flowchart.....	19
Fig. 4.2 Synthesis of a Heat-exchanger Network.....	22
Fig. 4.3 General Temperature Interval Diagram.....	28
Fig. 4.4 General Cascade Diagram.....	32
Fig. 4.5 General Revised Cascade Diagram.....	33
Fig. 4.6 Cost-benefit Analysis for Heat Exchangers.....	34
Fig. 5.1 Urea Manufacture—Partial Ammonia Recycle Process.....	41
Fig. 5.2 Current Heat-Exchange Network.....	44
Fig. 5.3 Temperature Interval Diagram.....	49
Fig. 5.4 Cascade Diagram.....	53
Fig. 5.5 Revised Cascade Diagram.....	54

	Page
Fig. 5.6 Matching the Streams.....	56
Fig. 5.7 The Grid Diagram for the Heat Exchange Network.....	57
Fig. 5.8 Matching the Streams After Cost-Benefit Analysis.....	58
Fig. 5.9 The Modified Grid Diagram for the Heat Exchange Network.....	60
Fig. 5.10 A Chlorine Consumed (Goldman et al. 1979).....	66
Fig. 5.10 B Chlorine Discharged (Goldman et al. 1979).....	67
Fig. 5.11 Reduction in Chlorine Added and Discharged.....	69
Fig. 5.12 Reduction in Seawater Flowrate.....	70
Fig. 5.13 Cost Savings Resulting From the Various Strategies.....	71

LIST OF TABLES

	Page
Table 4.1 Extracted Data for the Hot Streams.....	25
Table 4.2 Extracted Data for the Cold Streams.....	26
Table 4.3 Table of Exchangeable Loads for the Hot and Cold Streams.....	30
Table 5.1 Data for the Process Hot Streams.....	45
Table 5.2 Data for the Process Cold Streams.....	46
Table 5.3 Flowrate of Seawater in Process Coolers.....	47
Table 5.4 A Table of Exchangeable Loads for Hot Streams.....	50
Table 5.4 B Table of Exchangeable Loads for Cold Streams.....	51
Table 5.5 Chlorine Dosage and Consumption (Goldman et al. 1979).....	66
Table 5.6 Estimated Chlorine Discharge for Different Doses.....	67
Table 5.7 Added and Discharge Chlorine.....	68

NOMENCLATURE

Q^{HU}	Heating Utilities
$Q_{Original}^{HU}$	Original Heating Utility
$Q_{Reduction}^{HU}$	Currently Used Heating Utilities
$Q_{Reduction}^{HU}$	Reduction in Heating Utilities after Heat Integration
$Q_{Reduced}^{HU}$	Reduced Heating Utilities after Heat Integration
Q^{CU}	Cooling Utilities
$Q_{Original}^{CU}$	Original Cooling Utility
$Q_{Current}^{HU}$	Currently used Cooling Utilities
$Q_{Reduction}^{CU}$	Reduction in Cooling Utilities after Heat Integration
$Q_{Reduced}^{CU}$	Reduced Cooling Utilities after Heat Integration
$F^{S.W.}$	Seawater Flow Rate
$F_{Current}^{S.W.}$	Currently Used Seawater Flow Rate
$F_{Reduction}^{S.W.}$	Reduction in Seawater Flow Rate after Heat Integration
$F_{Reduced}^{S.W.}$	Reduced Seawater Flow Rate after Heat Integration
$F_{Revision}^{S.W.}$	Revision in Seawater Flow Rate after Revising Delta Temperature
$F_{Revised}^{S.W.}$	Revised Seawater Flow Rate after Revising Delta Temperature

F_{AHI}^{CU}	The Required Flowrate of Seawater after Heat Integration.
$F_{AHI\&TM}^{CU}$	The Required Flowrate of Seawater After Heat Integration and Temperature-span Maximization.
C_p	Specific Heat
$D^{Biocide}$	Dosage of Biocide as PPM or mg/L
$D_{Optimal}^{Biocide}$	Optimal Biocide Dosage
$\Delta T^{S.W.}$	Outlet Temperature Minus Inlet Temperature of Cooled Streams of Exchanger
$\Delta T^{SW,max}$	Maximum Outlet Temperature minus Inlet Temperature of cooled streams of Exchanger
$T^{SW,out\ max}$	Maximum Outlet Temperature of Seawater
T^{out}	Outlet Temperature of Exchanger
T^{in}	Inlet Temperature of Exchanger
$\Delta T_{Original}^{S.W.}$	The Original Outlet Temperature Minus Inlet Temperature of Cooled Streams of Exchanger
$\Delta T_{Revised}^{S.W.}$	The Revised The Original Outlet Temperature Minus Inlet Temperature of Cooled Streams of Exchanger
$\Delta T_{ThermalPollution}^{S.W.}$	Regulated $\Delta T^{S.W.}$ to Prevent High Temperatures Discharge Water to Sea
$L^{Biocide}$	The amount of Biocide Added/ Discharged

$L_{Current,in}^{Biocide}$	The Currently Added Amount of Biocide Added to Seawater
$L_{Regulated}^{Biocide}$	The Maximum Amount of Biocide Regulated to be Discharged to Sea
$L_{Reduction,in}^{Biocide}$	Reduction in Added Biocide Amount from Cooling Reduction.
$L_{Reduced,in}^{Biocide}$	Amount of Added Biocide Reduced from Cooling Reduction.
$L_{Revision,in}^{Biocide}$	Revision in Added Biocide Amount from Revising Discharged Seawater Temperature.
$L_{Revised,in}^{Biocide}$	Amount of Added Biocide Revised from Revising Discharged Seawater Temperature.
$L_{Adjustment,in}^{Biocide}$	Adjustment in Added Biocide Amount after Optimal Dosage of Biocide
$L_{Adjusted,in}^{Biocide}$	Adjusted Added Biocide Amount after Optimal Dosage of Biocide
$L_{Current,out}^{Biocide}$	The Currently Amount of Biocide Discharged to Seawater
$L_{Reduction,out}^{Biocide}$	Reduction in Biocide Discharged Amount from Cooling Reduction.
$L_{Reduced,out}^{Biocide}$	Amount of Discharged Biocide Reduced from Cooling Reduction.
$L_{Revision,out}^{Biocide}$	Revision in Discharged Biocide Amount from Revising Discharged Seawater Temperature.
$L_{Revised,out}^{Biocide}$	Amount of Discharged Biocide Revised from Revising Discharged Seawater Temperature.

$L_{Adjustment_{out}}^{Biocide}$	Adjustment in Discharged Biocide Amount after Optimal Dosage of Biocide
$L_{Adjusted_{out}}^{Biocide}$	Adjusted Discharged Biocide Amount after Optimal Dosage of Biocide
ΔH_1^H	Enthalpy Difference for Hot Streams at Temperature Interval One.
$\sum \Delta H^H$	The Summation of Enthalpy Differences for all Hot Streams.
ΔH_1^C	Enthalpy Difference for Cold Streams at Temperature Interval One.
$\sum \Delta H^C$	The Summation of Enthalpy Differences for all Cold Streams.

CHAPTER I

INTRODUCTION

The use of seawater in industrial cooling is a common practice in many parts of the world that have limited fresh-water resources. One of the primary operational problems of using seawater in cooling is biofouling. Because of the biological activities of micro-organisms in seawater, biofilms are formed. These biofilms tend to stick to heat-exchange surfaces, thereby significantly reducing heat-transfer coefficients. For instance, the heat-transfer coefficient may be reduced by 50% when a 250 μm thick biofilm is formed (Goodman 1987). In some cases, excessive bio-fouling can lead to plugging of heat exchangers. There are several techniques for preventing biofouling:

1. Biocide application: Disinfectants (El-Halwagi 1997; El-Halwagi et al. 1995) are added to reduce or eliminate the biological activities that contribute to biofouling and blacking of the cooling systems. Chlorine-based disinfection is the most widely used system because of relatively low cost and high effectiveness. Seawater may be chlorinated either by diffusing chlorine gas, electrolyzing seawater to produce chlorine, or adding a chlorinated solution such as sodium hypochlorite. Other forms of chlorinated disinfectants include chloramines (e.g., NH_2Cl , NHCl_2 , and NCl_3) and chlorine dioxide.

This dissertation follows the style of Clean Technologies and Environmental Policy.

2. There are other disinfectants such as ozone. However, it has not received broad commercial utilization because of the relatively high cost of ozonation and the risk factors associated with possible leakage. Ozone concentrations as low as 0.03 ppm are harmful to workers and surroundings if there is a leakage in the process.
3. Ultraviolet radiation: This is an effective disinfection method. However, its applicability is limited to cases when the water has little turbidity and suspended matter. Also, there is no residual disinfection effect after the radiation.
4. “Natural” disinfection: The key concept is to use natural disinfecting factors such light intensity, distribution, solar emission, salinity, temperature, and pH control for disinfection. (Yukselen et al. 2003) recommended the use of light intensity for disinfection. (Yang et al. 2000) conducted a study using these factor and examined their effect on e-coli in wastewater. They recommend the use of 60,000 lux of light intensity and salinity of 35% to reach T90 (90%) die-off of bacteria in 55 minutes. Natural disinfection reduces the extent of released harmful materials. However, much more work is needed for broad commercialization.
5. Reducing the tendency of biofilms to stick to heat-exchange surfaces. There are chemical and hydro-mechanical methods. The primary chemical method is the use of surfactants that reduce the adhesion forces of the biofilm to the surface of heat exchangers. The hydro-mechanical methods involve the enhancement of

turbulence of seawater flow within the heat exchangers to continuously or intermittently scrape the biofilms.

6. Using mechanical means (e.g., rotating brushes and sponge balls) for regular cleaning (Langford 1977).
7. Pulsating hot solutions (e.g. hot seawater) on a regular basis. The hot solution should be at a temperature hot enough to deactivate the micro-organisms.
8. Genetic and biological engineering to alter bio-sensing and inhibit the formation of biofilms.

Of the aforementioned techniques, biocide dosing (primarily chlorination) is the most widely-used approach. This is attributed to industrial reliability, large-scale applicability, effectiveness in disinfecting various forms on micro-organisms in seawater, and cost effectiveness. On the other hand, biocide usage on a large scale can result in serious environmental problems. Specifically, *chemical pollution* is the primary environmental problem associated with the use of biocide for disinfecting seawater used for cooling. After using biocide-laden seawater in cooling, it is discharged back to the sea. The discharged seawater contains unused biocide along with byproducts resulting from the application of the biocide. Most of the commercial disinfectants and their byproducts are in the form of chemicals that are harmful to the aquatic lives. For instance, a biocide (such as chlorine) may react with organics to form hazardous compounds such as trihalomethanes (THMs), halogenated acetic acids (HAAs), and halophenols (HPs) which are carcinogenic for human health and aquatic life (Yang et al. 2000).

Another environmental problem associated with the use of seawater for cooling is *thermal pollution*. As a result of using seawater in cooling, its temperature will increase. The temperature of the discharged seawater. If the temperature rise is significant, it can lead to thermal pollution of the receiving seawater. Thermal pollution can threaten the health and diversity of aquatic lives. Thermal pollution is by controlling the difference between the intake seawater temperature and the temperature of discharged seawater. This temperature difference is normally kept below 5-8°C and attention is paid to keep most discharges below 35 °C (Ma et al. 1998).

The foregoing discussion illustrates the significant need to study the environmental problems associated with the use of seawater cooling and to develop cost-effective strategies that limit the negative environmental impact of using seawater in cooling. This is the scope of this work. The objective of this work is to address the issue of seawater cooling systems and the associated environmental problems including chemical and thermal pollution. The conventional approach to resolve biocide discharge issues has been the utilization of biocide removal units (e.g., dechlorination using sodium bisulfite). This is an end-of-pipe treatment which does not take advantage of the opportunities associated with process modification and integration. An integrated approach will be developed to optimize the process needs for utility, reduce seawater flowrates, and minimize biocide-related environmental emissions while satisfying thermal-pollution constraints. Chapter II provides a brief literature review on biocide addition and basic aspects of seawater chemistry. Chapter III is a formal statement of the problem. Chapter

IV introduces the process integration methodology along with the necessary computational tools. A case study on the use of seawater in cooling a urea plant is analyzed in Chapter V. Conclusions and recommendations for future work are given by Chapter VI.

CHAPTER II

LITERATURE REVIEW

This chapter provides a selective review of relevant literature. In particular, focus is given to chlorine-based systems since they chlorine is the most-commonly used biocide. Chemical pathways, species distribution, and kinetics will be quickly reviewed.

2.1. BIOCIDES DOSAGE

The typical once-through seawater cooling systems begin with screening seawater from blockages. Then, seawater is pumped to retention basins where chemical treatment can be applied. Typically, the biocide is dispersed through the seawater through mechanical means. For instance, chlorine may be added through diffusers that distribute chlorine in the form of fine bubble with high rates of mass transfer. There are three main strategies for biocide addition: continuous, pulse, and shock (Grant & Bott 2003). Continuous biocide addition involves a steady dosage over an extended period of time. Pulse dosing is an evenly-spaced intermittent form where the biocide is frequently added. Shock dosing (or super-dosing) uses relatively high dosage “bursts” of biocide addition. The dosage is typically higher in concentration and lower in frequency than pulse dosing.

The most commonly used biocide is chlorine. Different ways are used to produce chlorine. In many cases, it is a key of chlor-alkali industries. Electro-dialysis of brine is

also a commercial method for producing chlorine. Chlorine may also be produced through electro-chlorination. For instance, in Hong Kong more than 60% of the chlorine is produced from seawater by electro-chlorination in continuous basins to produce dosages of 0.2-2.0 mg/L of free chlorine (Ma et al. 1998). The following section discusses the key aspects of chlorine usage as a biocide.

2.2. BASIC CHEMISTRY OF CHLORINE-BASED DISINFECTION

When chlorine is added to seawater, the following reactions take place:



where HOCl is hypochlorous acid. This reaction is extremely fast (almost instantaneous). The formed hypochlorous acid further dissociates as follows:



where OCl^- is the hypochlorite ion. Reaction (2.1) is extremely fast while reaction (2.2) is slow. Because of the presence of H^+ in the second reaction, the distribution of the various species at equilibrium is a function of pH. Figure 2.1. is an illustration of the effect of pH on the species distribution. In terms of disinfection effectiveness, hypochlorous acid is much stronger (almost two orders of magnitude) than the hypochlorite ion.

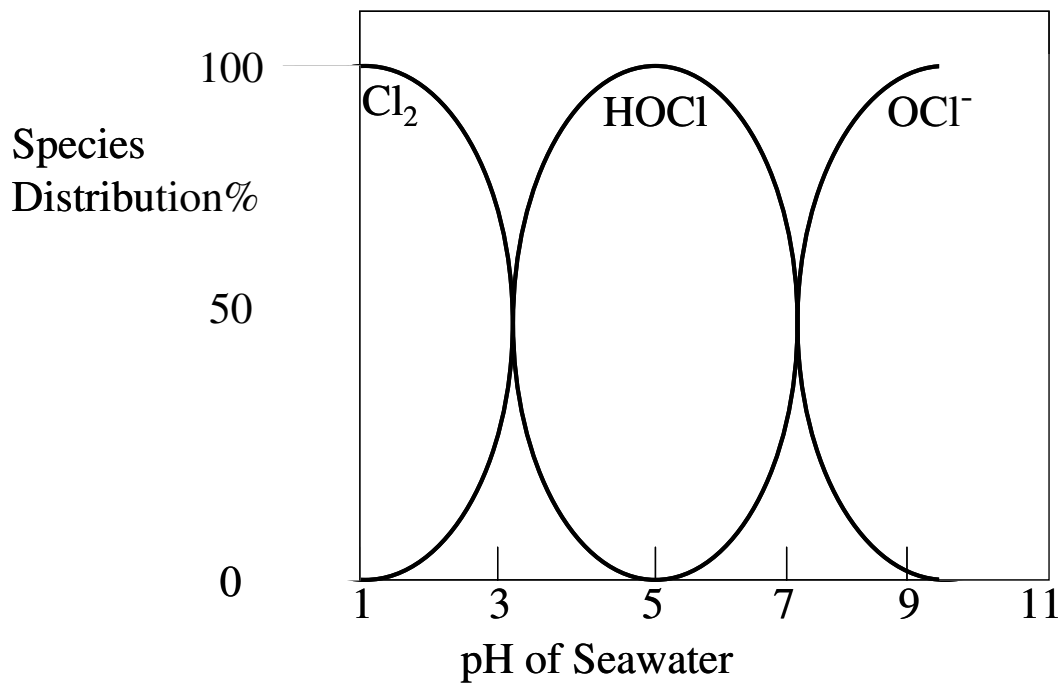


Fig. 2.1 Chlorination-Species Distribution as a Function of pH (Based on Data by (Oldfield & Todd 1981))

If the seawater contains ammonia or other reactive nitrogenous compounds, these species may be chlorinated to give monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramine (NCl_3). These combined forms consume free chlorine and deprive it from being available for disinfection. Such combined forms are much less effective biocides than the free forms. Therefore, it is important to distinguish between two definitions of chlorine concentrations:

$$\text{Free residual chlorine "FRC"} = 2[\text{Cl}_2] + [\text{HOCl}] + [\text{OCl}^-] \quad (2.3)$$

These are the free forms available for disinfection. Most of the time, the concentration of Cl_2 is negligible because of its fast reaction to form HOCl. On the other hand,

$$\text{Total residual chlorine "TRC"} = \text{FRC} + [\text{NH}_2\text{Cl}] + 2[\text{NHCl}_2] + 3[\text{NCl}_3] \quad (2.4)$$

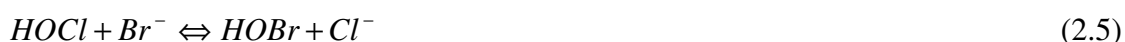
Normally, the concentration of NCl_3 is negligible.

Residual chlorine concentration is typically measured through the DPD (diethyl phenylene diamine) method. It is a colorimetric method based on the formation of a pink color when DPD reacts with oxidized forms of chlorinated compounds (e.g., HOCl, OCl, NH_2Cl , etc.). This method does not yield color change for the chloride ionic form which is abundant in seawater and should be distinguished from active chlorine forms. Note that the chloride ion (Cl^-) does not induce a color change. The DPD method can be tailored to measure free chlorine (HOCl and OCl) or combined chlorine (including chloramines).

2.3. BROMIDE- AND BROMINE-BASED DISINFECTION

It is also important to consider the effect of bromide which naturally exists in seawater.

Hypochlorous acid rapidly reactive with bromide as follows:



where HOBr is hypobromous acid. Additionally, the hypochlorite ion may undergo a slow reaction with the bromide ion as follows:



where OBr^- is the hypobromite ion. Bromide in seawater may also react directly with added chlorine to give bromine and chloride:



When seawater has higher bromide concentration, other reactions occur:



and



Bromine may also be used as a biocide. It reacts in water in a very comparable way to chlorine as follows:



Because of the presence of H^+ in the second reaction, the distribution of the various species at equilibrium is a function of pH. Figure 2.2. is an illustration of the effect of pH on the species distribution. Seawater is typically alkaline. Typical values of pH is about 8.2 for surface seawater and 7.5 for deep seawater (Goodman 1987). It is worth noting that for the range of pH of 7.5 to 8.2, the predominant form is HOBr. This is important since HOBr is the most active disinfectant species among the three forms.

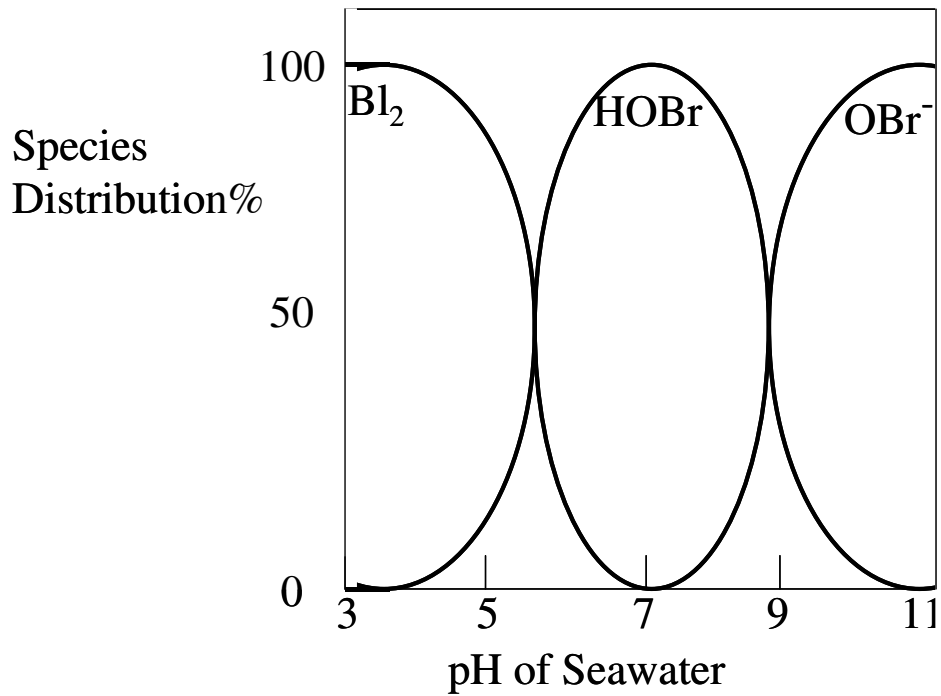


Fig. 2.2 Bromination-species Distribution as a Function of pH (Based on Data by (Oldfield & Todd 1981))

2.4. DISINFECTION KINETICS

The rate of disinfection reactions may be modeled in a variety of ways. The simplest model is the first-order kinetic model referred to as Chick law which establishes a relationship between disinfection rate of microorganisms by a biocide as:

$$r = -kN \quad (2.10)$$

where r is the rate of inactivation (number of micro-organisms disinfected/ volume-time), k is the reaction rate constant (1/time), and N is the concentration of active microorganisms (Hass & ASCE).

Later, Watson characterized k as a function of the disinfectant concentration (C):

$$k = k' C^n \quad (2.11)$$

where k' is the reaction rate constant which is independent of the disinfectant concentration, C is the disinfectant concentration, n is the dilution coefficient.

More advanced models can be found in literature. For instance, an empirical model was proposed by (Hom 1972) which takes the following form:

$$\frac{dN}{dt} = -kNC^m t^{h-1} \quad (2.12)$$

where N is the survival number of microorganisms, k is the disinfection rate constant, C is biocide concentration, m is Hom dilution coefficient, t is time, h is Hom time exponent (Lambert & Johnston 2000).

CHAPTER III

PROBLEM STATEMENT

The problem to be addressed in the work can be formally stated as follows: Given a process which uses seawater for cooling. In order to prevent biofouling in coolers, a biocide (e.g., chlorine) is added to the incoming seawater. The process intake of seawater is referred to as $F_{S.W.}^{Intake}$ and the load of added biocide is designated by $L_{Biocide}^{Intake}$.

Currently, the process discharges a flowrate, $F_{S.W.}^{Discharge}$, of used seawater and a biocide concentration of $C_{Biocide}^{Discharge}$ leading to a discharge load of biocide being

$$L_{Biocide}^{Discharge} = F_{S.W.}^{Discharge} * C_{Biocide}^{Discharge}.$$

Because of environmental regulations, it is desired to

reduce the load of discharged biocide to $L_{Biocide}^{Regulated}$. The objective is to develop a cost-effective procedure which integrates the process resources, revises process design and/or operation, and incorporates new technologies to meet the new regulation.

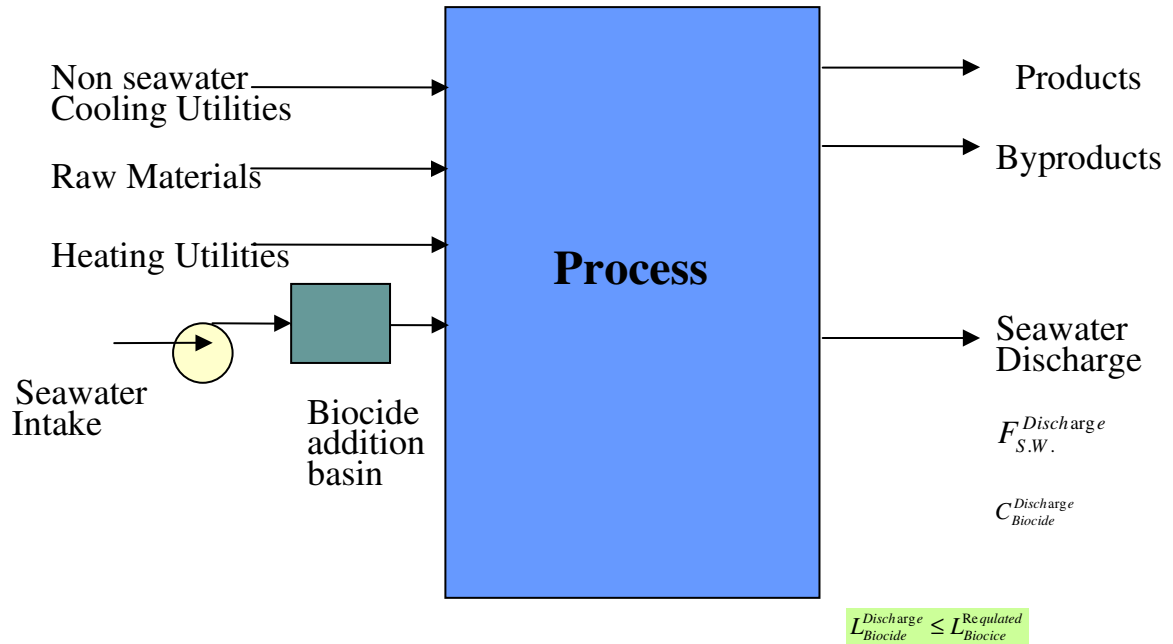


Fig. 3.1 A Schematic Representation of the Stated Problem

The abovementioned problem involves addressing the following challenges:

1. Seawater usage is linked to process requirements including cooling utilities. Reduction of cooling requirements has a direct impact on the amount of used and discharged seawater along with the used and discharged biocide.
2. Several design and operational changes can be made to reduce seawater usage and/or biocide load.
3. New biocide removal units (e.g., dechlorination) units may be added. These units should be screened according to techno-economic criteria.

These challenges call for the development and application of an integrated approach which addresses these highly interactive tasks while identifying cost-effective solutions.

This approach will be developed and applied in the ensuing chapters.

CHAPTER IV

THEORETICAL STUDY AND DESIGN APPROACH

4.1. RATIONALE AND OVERVIEW OF PROPOSED DESIGN PROCEDURE

Before developing the design approach to tackle the stated problem, it is beneficial to discuss the conventional engineering approach to addressing pollution problems arising from the discharge of biocide-laden cooling seawater. Typically, this problem will be solved using an “end-of-pipe” approach. Biocide removal units are added to treat cooling seawater prior to discharge. For instance, when chlorine is used as a biocide, dechlorination units are used to treat seawater and reduce the discharge of chlorine. Although this end-of-pipe solution works, the question is whether or not there can be superior solutions? The answer is that it is possible to find more cost-effective solutions if a holistic approach is adopted. The proposed approach is based on the following observations:

1. Reduction of cooling duties of the process will result in a lower usage and discharge of seawater. Consequently, the discharge of biocide will be reduced. An added advantage of reducing the cooling duties is that the utility cost is reduced leading to economic savings while preventing pollution.

2. More effective heat transfer can be used to reduce the flowrate of cooling seawater and, therefore, lower the discharge of biocide.
3. Biocide dosage should be optimized to achieve the desired process effects while minimizing the environmental discharge.
4. Biocide removal units (e.g., dechlorination) should be considered. However, the extent of biocide removal should be reconciled with the other alternatives such as reduction of cooling duties, reduction of seawater flowrate, and optimization of biocide dosage.

The foregoing observations constitute the basis for the proposed design procedure. First, effort will be made to reduce the cooling duty of the process. In this regard, heat integration can be instrumental. The rationale for starting with heat integration is that it can lead to cost savings by virtue of reducing cooling and heating utilities. This is a superior approach to end-of-pipe which regards biocide pollution abatement as an additional cost. Heat integration can generate cost savings while reducing the usage and discharge of seawater and biocide. Once heat integration is performed and a new cooling duty is determined, the reduced flowrate of seawater is calculated.

The next step in the procedure is to further reduce the flowrate of cooling seawater by enhancing the efficiency of seawater utilization. A relatively easy technique is to maximize the temperature range of seawater through the process. For a given inlet temperature of seawater, this technique corresponds to maximizing the outlet

temperature of seawater leaving the process while complying with environmental regulations on thermal pollution. A new flowrate of seawater can now be calculated.

The following step is to optimize the dosage of biocide added to incoming seawater such that the biocide achieves the desired process effects of preventing the bio-fouling while minimizing the discharge of biocide leaving the process.

The previous steps offer cost savings while reducing the biocide usage and discharge. Once these steps are exhausted, end-of-pipe treatment is used to reach the environmental target. For instance, biocide removal units (e.g., dechlorination devices) are added to treat the seawater leaving the plant and reduce the biocide load prior to environmental discharge. When multiple end-of-pipe are alternatives, they should be screened so as to select the cheapest alternative. Figure 4.1. is a schematic representation of the design flowchart summarizing the key steps in the procedure.

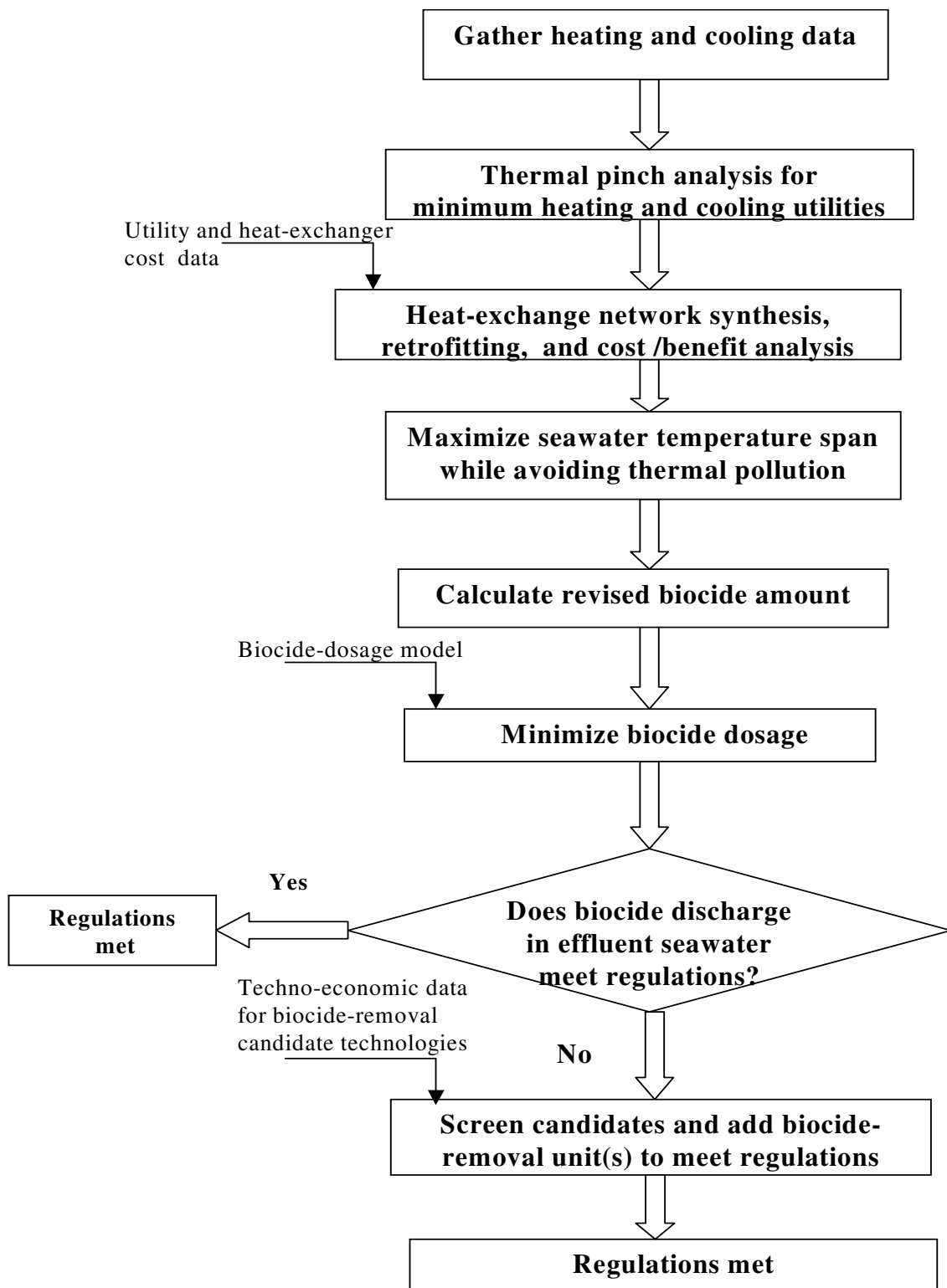


Fig. 4.1 Design Flowchart

4.2. HEAT INTEGRATION ANALYSIS

Consider a given plant whose current requirements of cooling and heating utilities are $Q_{Original}^{CU}$ and $Q_{Original}^{HU}$, respectively. Let us focus on the case when seawater is used to provide the cooling duties. This is the case when all cooling tasks requires temperatures that are least 5°C degrees above the seawater temperature. If lower temperatures are needed, refrigerants may be used. The flowrate of the seawater is related to the cooling utility through the following heat balance:

$$Q_{Original}^{CU} = F_{Original} * C_p * \Delta T_{Original}^{SW} \quad (4.1)$$

where $F_{Original}$ is the current flowrate of the cooling seawater, C_p is the heat capacity of the seawater, and $\Delta T_{Original}^{SW}$ is the current temperature difference (outlet temperature – inlet temperature) for seawater.

The first step in the heat integration analysis is to collect data on heat duties of all the heat exchangers along with temperature range. The idea behind heat integration techniques is to integrate heat within the process by transferring heat from process hot streams to process cold streams. The goal is to maximize the heat transfer from process hot streams to process cold streams so as to minimize the external cooling and heating utilities.

Once the minimum utility requirement is determined, the number of heat exchangers is minimized while achieving the desired heat-transfer steps. There are several rigorous techniques for synthesizing cost-effective heat-exchange networks “HENs” where heat is optimally exchanged among process hot and cold streams and the use of utilities is kept at a minimum. One of these techniques is the thermal pinch analysis (Linnhoff & Hindmarsh 1983). The HEN synthesis problem can be defined as follows: “Given a number of process hot streams (to be cooled) and a number of process cold streams (to be heated), it is desired to synthesize a cost-effective network of heat exchangers that can transfer heat from the hot streams to the cold streams. Given also are the heat capacity (flowrate \times specific heat) of each process hot stream, its supply (inlet) temperature, and its target (outlet) temperature. In addition, the heat capacity, supply and target temperatures, are given for each process cold stream. Available for service are several heating and cooling utilities whose supply and target temperatures (but not flowrates) are known.” Figure 4.2 is a schematic representation of the HEN problem statement.

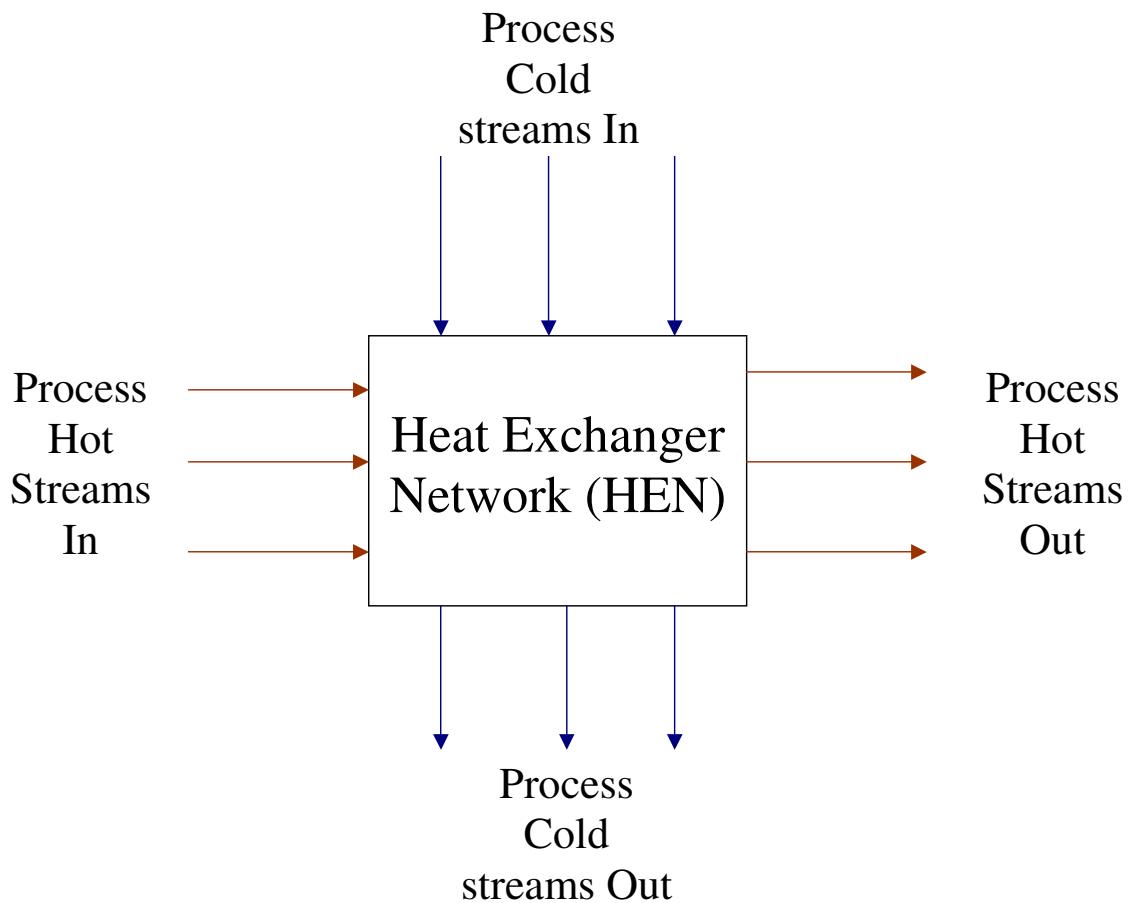


Fig. 4.2 Synthesis of a Heat-exchanger Network

Several graphical, algebraic, and mathematical methods have been developed for thermal pinch analysis. These methods have been reviewed by (El-Halwagi 1997) and (Shenoy 1995). One of the most computationally-effective techniques is the algebraic thermal-pinch analysis. The following is a brief summary of the steps. These steps will be explained in more details later.

1. Gather data on process hot and cold streams. Get the flowrate, heat capacity, supply temperature, and target temperature for each stream. These data can be used to calculate the heating and cooling duty of each stream.
2. Construct a temperature interval diagram for the hot and cold streams where each stream is represented as an arrow extending between supply and target temperatures. The hot streams are represented versus a hot scale while the cold streams are represented versus a cold scale. The hot and the cold temperature scales are separated by a minimum temperature driving force. The temperature span between each two temperatures is referred to as a temperature interval.
3. Develop a cascade diagram where heat balances are carried out around the temperature intervals. Residual heat loads are passed from an interval to the next one. A negative residual corresponds to an infeasible heat exchange. The most negative residual corresponds to the minimum heating utility which should be added to the top of the cascade. The heat balances are revised accordingly and the residual heat leaving the last temperature interval corresponds to the minimum cooling utility. The location where the residual heat is zero is the thermal-pinch temperature.
4. No heat should be passed from below or above the pinch to maintain the minimum utilities usage.
5. Build a heat exchanger network for above and below the pinch. From this network the minimum number of exchangers can be calculated.

One of the critical steps in the synthesis of the HEN is the proper data extraction of heating and cooling utilities. In this context, heat duties for all the hot streams to be cooled and all the cold streams to be heated must be collected. Units that require heating or cooling are also incorporated.

Additionally, existing exchangers that use heating or cooling utilities are considered in the analysis after they are detached from the current utility usage. Later, optimal utility usage and allocation will be determined. For each hot and cold streams, the extracted data are expressed in terms of flowrate, specific heat, supply and target temperatures, and heat loads. Tables 4.1. and 4.2. illustrate these tables for the hot and the cold streams. The total loads of heating and cooling utilities are calculated at the bottom of each table. These represent the current usage of the heating utility in Table 4.2 and cooling utility in Table 4.1 for the process.

Table 4.1 Extracted Data for the Hot Streams

Heat Exchanger Hot Streams	$F^H * Cp^H$	T_{Supply}^H	T_{Target}^H	Heat Load
HE-1	$F_1^H * Cp_1^H$	$T_{Supply,1}^H$	$T_{Target,1}^H$	$F_1^H * Cp_1^H (T_{Supply,1}^H - T_{Target,1}^H)$
HE-2	$F_2^H * Cp_2^H$	$T_{Supply,2}^H$	$T_{Target,2}^H$	$F_2^H * Cp_2^H (T_{Supply,2}^H - T_{Target,2}^H)$
HE-3	$F_3^H * Cp_3^H$	$T_{Supply,3}^H$	$T_{Target,3}^H$	$F_3^H * Cp_3^H (T_{Supply,3}^H - T_{Target,3}^H)$
....
...
...
HE-n	$F_n^H * Cp_n^H$	$T_{Supply,n}^H$	$T_{Target,n}^H$	$F_n^H * Cp_n^H (T_{Supply,n}^H - T_{Target,n}^H)$
Total				$\sum \Delta H^H = Q_{Current}^{CU}$

Table 4.2 Extracted Data for the Cold Streams

Heat Exchanger Cold Streams	$F^C * Cp^C$	T_{Supply}^C	T_{Target}^C	Heat Load
HE-1	$F_1^C * Cp_1^C$	$T_{Supply,1}^C$	$T_{Target,1}^C$	$F_1^C * Cp_1^C (T_{Supply,1}^C - T_{Target,1}^C)$
HE-2	$F_2^C * Cp_2^C$	$T_{Supply,2}^C$	$T_{Target,2}^C$	$F_2^C * Cp_2^C (T_{Supply,2}^C - T_{Target,2}^C)$
HE-3	$F_3^C * Cp_3^C$	$T_{Supply,3}^C$	$T_{Target,3}^C$	$F_3^C * Cp_3^C (T_{Supply,3}^C - T_{Target,3}^C)$
...
...
....
HE-m	$F_m^C * Cp_m^C$	$T_{Supply,m}^C$	$T_{Target,m}^C$	$F_m^C * Cp_m^C (T_{Supply,m}^C - T_{Target,m}^C)$
Total				$\sum \Delta H^C = Q_{Current}^{HU}$

The next step is to construct a temperature interval diagram (TID) which represents all the hot and cold streams. Two temperature axes are used: one for hot and one for cold. The two scales are separated by a minimum driving force which is referred as: ΔT^{\min} . The minimum deriving force usually in the range of $(5-10)^{\circ}C$, which corresponds to $(9-18)^{\circ}F$. The hot streams are represented in the actual temperature values. But the cold streams should have the minimum approach temperature less than the corresponding hot stream temperature.

On the TID, each stream is represented by an arrow extending between supply and target temperatures. Horizontal lines are drawn at heads and tails of arrows. These horizontal lines constitute temperature intervals. This diagram is not on scale because it represents on the temperature intervals for hot and cold streams. Figure 4.3. is a schematic illustration of a TID.

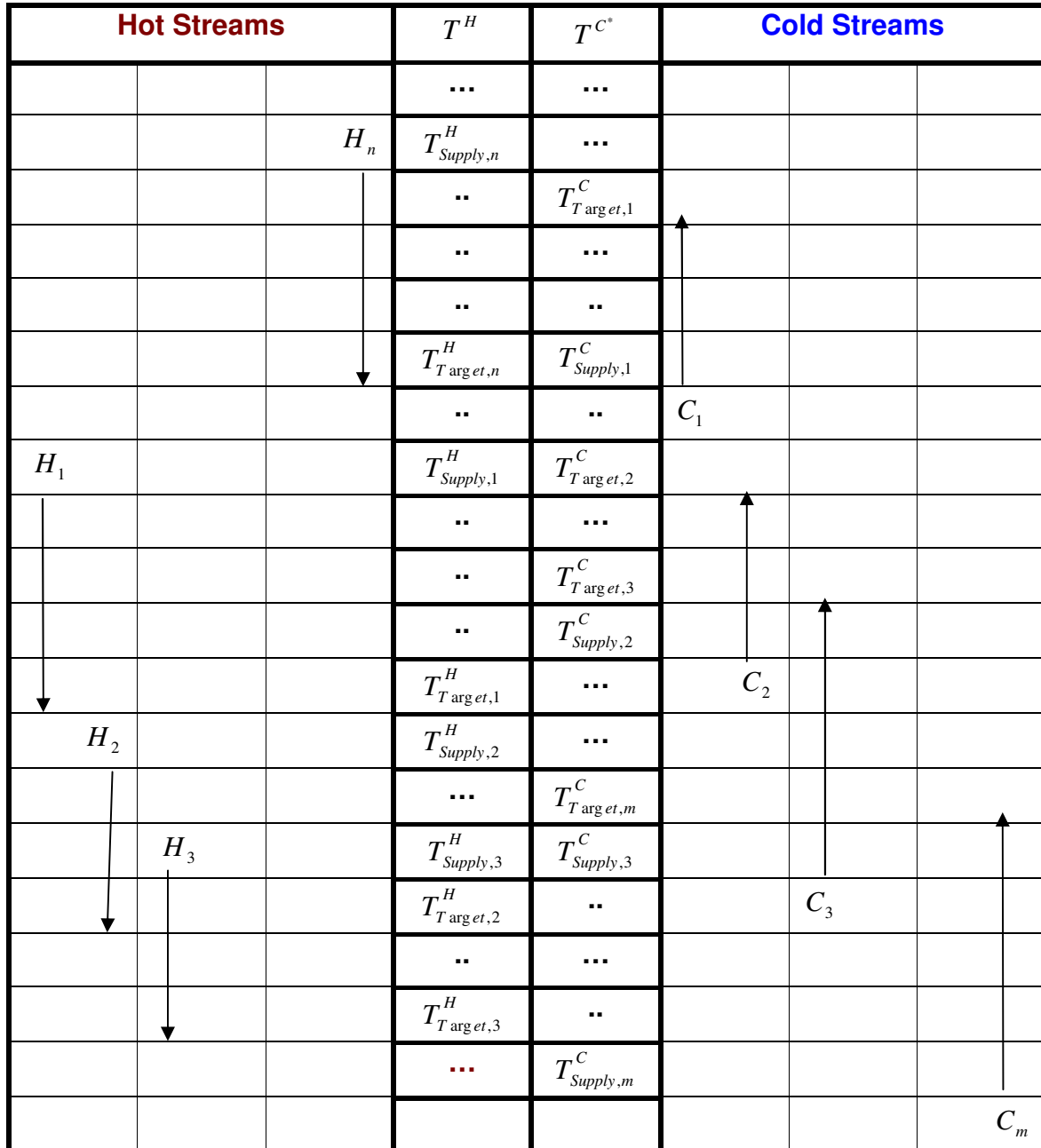


Fig. 4.3 General Temperature Interval Diagram

In order to calculate the Enthalpy for each stream at each temperature interval, the table of exchangeable loads is developed. If a hot or cold stream passes through a temperature interval, then its enthalpy in that interval is calculated. Otherwise, it is assigned a zero enthalpy change. The enthalpy is calculated by multiplying the temperature interval difference by the specific heat and the flow rate of the fluid. As shown in the below equation:

$$Q^{CU} = F^{CU} * C_p \Delta T^{CU}$$

Figure 4.4. is a representation of the table of exchangeable loads for the hot and cold Streams. The result of adding the exchangeable heat load horizontally for hot streams should represent the heat required to be removed from the hot streams. If all heat required to be removed are summed should equal to the cooling utility. The same is for cold streams. If all heat required to be added to the cold streams are summed, they should equal to the heating utility.

Table 4.3 Table of Exchangeable Loads for the Hot and Cold Streams

Intervals	C_1	C_2	C_3	C_m	Total
1	$\Delta H_1^{C_1}$	$\Delta H_1^{C_2}$	$\Delta H_1^{C_3}$	$\Delta H_1^{C_m}$	ΔH_1^C
2	$\Delta H_2^{C_1}$	$\Delta H_2^{C_2}$	$\Delta H_2^{C_3}$	$\Delta H_2^{C_m}$	ΔH_2^C
3	$\Delta H_3^{C_1}$	$\Delta H_3^{C_2}$	$\Delta H_3^{C_3}$	$\Delta H_3^{C_m}$	ΔH_3^C
..
..
..
Z	$\Delta H_z^{C_1}$	$\Delta H_z^{C_2}$	$\Delta H_z^{C_3}$	$\Delta H_z^{C_m}$	ΔH_z^C
Total								$\sum \Delta H^C$

Intervals	H_1	H_2	H_3	H_n	Total
1	$\Delta H_1^{H_1}$	$\Delta H_1^{H_2}$	$\Delta H_1^{H_3}$	$\Delta H_1^{H_n}$	ΔH_1^H
2	$\Delta H_2^{H_1}$	$\Delta H_2^{H_2}$	$\Delta H_2^{H_3}$	$\Delta H_2^{H_n}$	ΔH_2^H
3	$\Delta H_3^{H_1}$	$\Delta H_3^{H_2}$	$\Delta H_3^{H_3}$	$\Delta H_3^{H_n}$	ΔH_3^H
..
..
..
Z	$\Delta H_z^{H_1}$	$\Delta H_z^{H_2}$	$\Delta H_z^{H_3}$	$\Delta H_z^{H_n}$	ΔH_z^H
Total								$\sum \Delta H^H$

With all the temperature intervals and their exchangeable loads determined, the cascade diagram is developed for the problem. The cascade diagram includes all the temperature intervals. The hot loads are added as inputs from the left and the cold loads are added as outputs to the right. The hot loads are the enthalpy differences for the hot streams at the temperature interval. And the cold loads are the enthalpy difference for cold streams at the same temperature interval. The hot loads are counted as inputs because they are the source of the heat and cold loads are the outputs because they are receiving the heat. Heat balances are carried out around the intervals to determine the residual heats (Fig. 4.4).

Negative residual heats indicate thermodynamic infeasibility. Therefore, the most negative residual heat is added from the top. This constitutes the minimum heating utility. The residual heats are re-calculated and the last residual heat leaving the cascade corresponds to the minimum cooling utility. This is shown by Fig. 4.5.

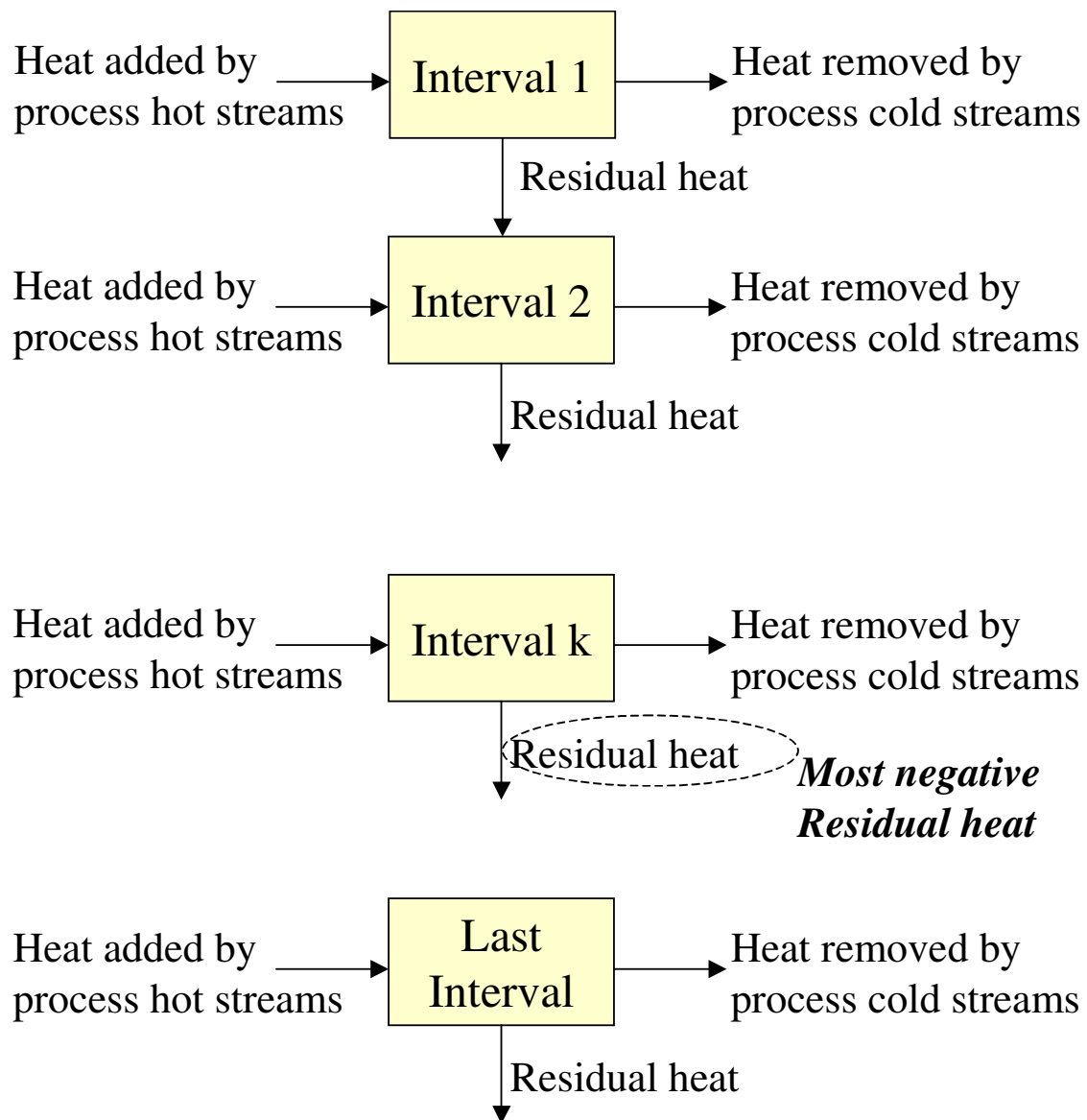


Fig. 4.4 General Cascade Diagram

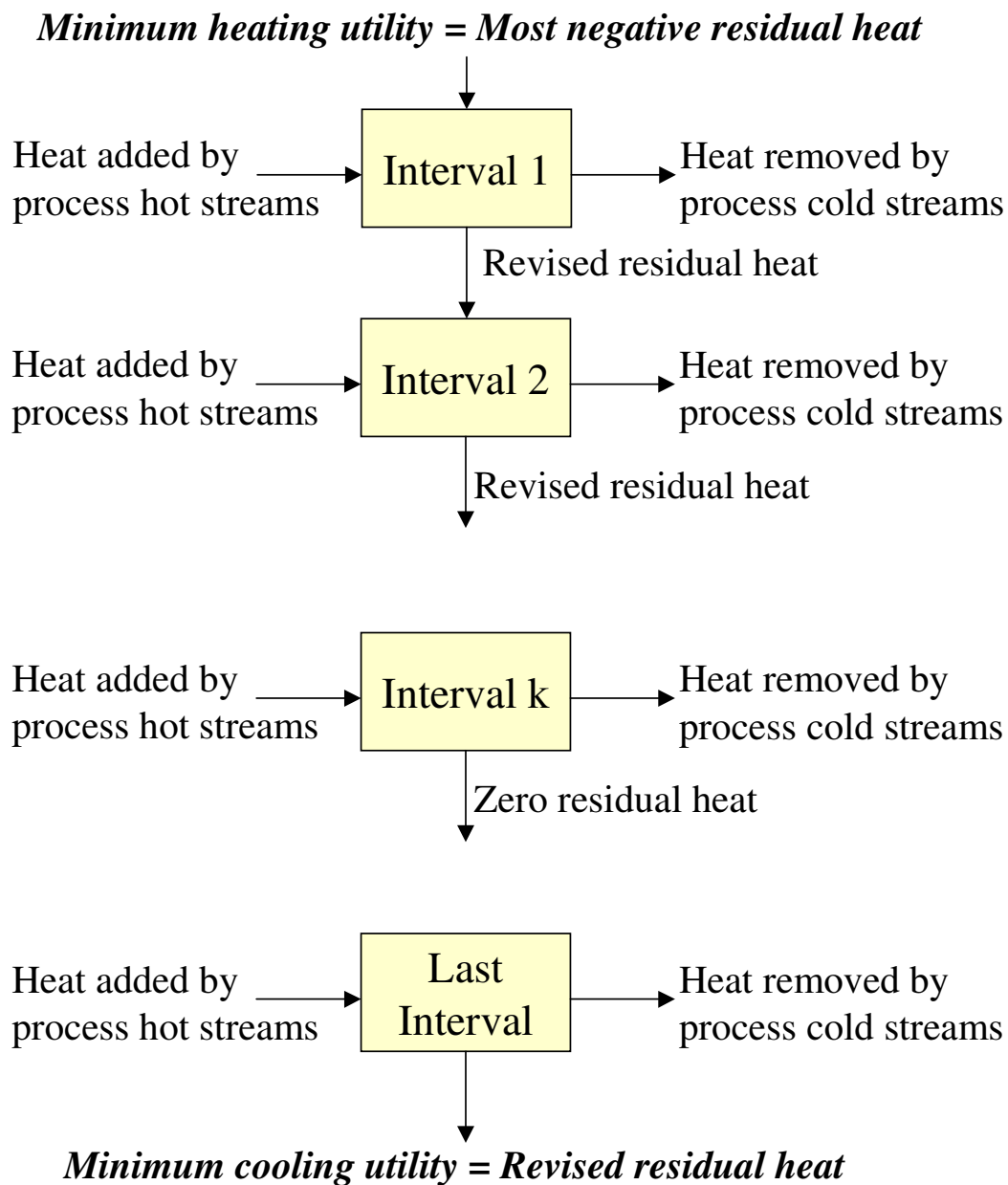


Fig. 4.5 General Revised Cascade Diagram

In retrofitting the heat exchangers, it is necessary to insure that the cost savings resulting from the heating and cooling utilities exceed any additional capital cost of the heat

exchangers. Some of the economic criteria used include return on investment (ROI). Figure 4.6. is a schematic representation of the cost-benefit analysis for the heat exchangers.

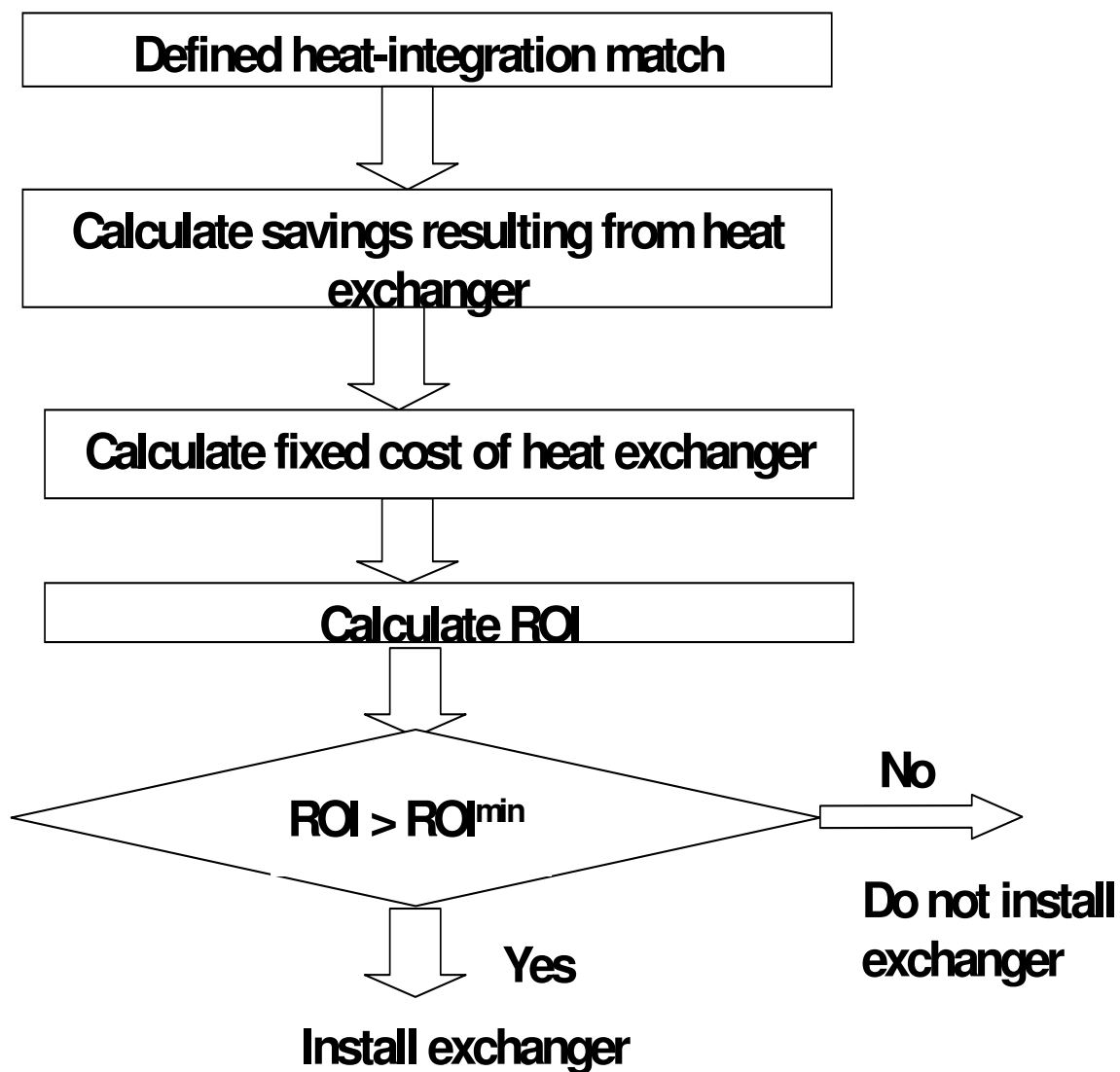


Fig. 4.6 Cost-benefit Analysis for Heat Exchangers

The heat-integration analysis results in the identification of the minimum cooling utility.

Let us refer to it as cooling utility after heat integration, Q_{AHI}^{CU} . This

$$Q_{AHI}^{CU} = F_{AHI}^{CU} * C_P * \Delta T_{Original}^{SW} \quad (4.2a)$$

or

$$F_{AHI}^{CU} = \frac{Q_{AHI}^{CU}}{C_P * \Delta T_{Original}^{SW}} \quad (4.2b)$$

where F_{AHI}^{CU} is the required flowrate of seawater after heat integration. Since the cooling duty has been reduced as a result of heat integration, the required flowrate of seawater after heat integration will also decrease. Indeed, the ratio of the seawater after heat integration and before heat integration is expressed as follows:

$$\frac{F_{AHI}}{F_{Original}} = \frac{Q_{AHI}^{CU}}{Q_{Original}^{CU}} \quad (4.3)$$

Once the heat exchange duties for the hot and cold streams are determined, the existing network of heat exchangers is retrofitted to satisfy the required heating duties. In matching streams, no heat should be passed through the pinch otherwise the heating and cooling utilities will increase. In deciding whether or not a new heat exchanger should be added, a cost-benefit analysis should be undertaken. Based on this analysis, the considered heat exchangers are the ones that save utility cost and associated waste disposal cost large enough to justify the investment of a new heat exchanger.

The cost savings associated with the reduction in heating and cooling utilities can be calculated as follows:

Annual savings from heat integration = Annual savings from reduction in heating utilities + Annual savings from reduction in cooling utilities - Annualized fixed cost of additional heat exchangers.

Furthermore, there are additional savings attributed to the reduction in the treatment cost of effluent seawater and the removal of remaining biocides before discharge.

4.3. MAXIMIZATION OF TEMPERATURE SPAN

Recalling Eq. (4.2b), it can be seen that

$$F_{AHI}^{CU} = \frac{Q_{AHI}^{CU}}{C_P * \Delta T_{Original}^{SW}} \quad (4.4)$$

Therefore, in order to further reduce the flowrate of the seawater the term $\Delta T_{Original}^{SW}$ should be maximized. This temperature designates the difference between outlet and inlet temperature of seawater, i.e.

$$\Delta T_{Original}^{SW} = T_{Original}^{SW,out} - T_{Original}^{SW,in} \quad (4.5)$$

For the case when the inlet seawater temperature is given, then maximizing the temperature span corresponds to maximizing the outlet temperature of seawater, i.e.

$$\Delta T^{SW, \max} = T^{SW, out \max} - T_{Original}^{SW, in} \quad (4.6)$$

In maximizing the temperature span for seawater care must be given to stay below the environmentally-regulated limit beyond which thermal pollution may occur, i.e.

$$\Delta T^{SW, \max} \leq \Delta T^{SW, Thermal \ Pollution} \quad (4.7)$$

Now, the heat balance can be written as:

$$Q_{AHI}^{CU} = F_{AHI \& TM}^{CU} * C_p * \Delta T^{SW, \max} \quad (4.8 \ a)$$

or

$$F_{AHI \& TM}^{CU} = \frac{Q_{AHI}^{CU}}{C_p * \Delta T^{SW, \max}} \quad (4.8 \ b)$$

where $F_{AHI \& TM}^{CU}$ is the required flowrate of seawater after heat integration and temperature-span maximization. The reduction in seawater flowrate leads to reduction in the usage of biocide as well as reduction in treatment cost of discharged wastewater. Both translate into cost savings.

4.5. DOSAGE OPTIMIZATION

In this step, the chemical dosage of biocide is optimized. The objective is to use the smallest feasible dosage that achieves the process tasks of preventing bio-fouling at an appropriate level. In this step, understanding of the stoichiometry and kinetics of chemical and biological reactions is needed to adjust the dosage. Furthermore, the relationship between the dosage and the design and operational changes (e.g, effect of turbulence, maintenance schedule, tube cleaning, etc.). should be established to minimize the dosage. There are three main strategies for biocide addition: continuous, pulse, and shock (Grant & Bott 2003). Continuous biocide addition involves a steady dosage over an extended period of time. Pulse dosing is an evenly-spaced intermittent form where the biocide is frequently added. Shock dosing (or super-dosing) uses relatively high dosage “bursts” of biocide addition. The dosage is typically higher in concentration and lower in frequency than pulse dosing. The modeling result is that dosage can be related to seawater characteristics, design, and operating variables as follows:

$$\text{Dosage} = f(\text{seawater characteristics, design variables, operational variables}) \quad (4.9)$$

This function can be minimized so as to identify the minimum acceptable dosage of biocide that satisfies the process operation and to determine the necessary changes in design and operating variables to reach this minimum. If the dosage is continuous, then Eq. (4.9) is an algebraic system that can be minimized by conventional optimization

techniques. However, for pulse and shock dosing, then the dosage model is a dynamic system of algebraic and partial differential equations. The development of this dynamic model should include a time-based tracking of the biocide chemistry and propagation, impact on bio-fouling, as well as dynamic performance of the process. Because of the nonlinear, nonconvex, and dynamic nature of this model, its global minimization is a challenging task and is beyond the scope of this work.

4.6. END-OF-PIPE TREATMENT

The previous solution strategies result in dual benefits: cost savings as well as reduction in biocide discharge. If the desired discharge limit is achieved, the procedure is stopped. Otherwise, a biocide removal unit (e.g., dechlorination device) is added to treat the effluent seawater before discharge and to reach the desired limit of biocide discharge. The removal load is the discharged load after heat integration, temperature maximization, and dosage optimization minus the desired discharge load.

If multiple biocide removal technologies are technically feasible, economic screening is used to select the most cost effective technology. The cost data for each technology need to be collect. Then, compute the annualized cost for removing mass biocide. For instance, when several candidate technologies are thermodynamically feasible, the biocide-removal alternative with the least cost per unit mass removed should be selected.

CHAPTER V

CASE STUDY AND DISCUSSION OF RESULTS

In this chapter, a case study is solved on the optimization of seawater cooling and chlorination for a urea production process. First, the flowsheet is described and the relevant data are summarized. Then, the developed procedure is applied to the case study. The results are analyzed and discussed.

5.1 PROCESS DESCRIPTION

Figure 5.1 is a schematic representation of the process flowsheet for the urea production process. The key feedstock is ammonia and it is produced from a nearby ammonia plant. Liquid ammonia at $-28^{\circ}F$ is pumped to the reactor. Additionally, liquid ammonia is recycled from the ammonia separator and is pumped to the bottom reactor. Carbon dioxide gas is fed as well to the bottom of the reactor after cooling to $100^{\circ}F$ and after being compressed to 3,515 psia through four stages of compressors and five coolers.

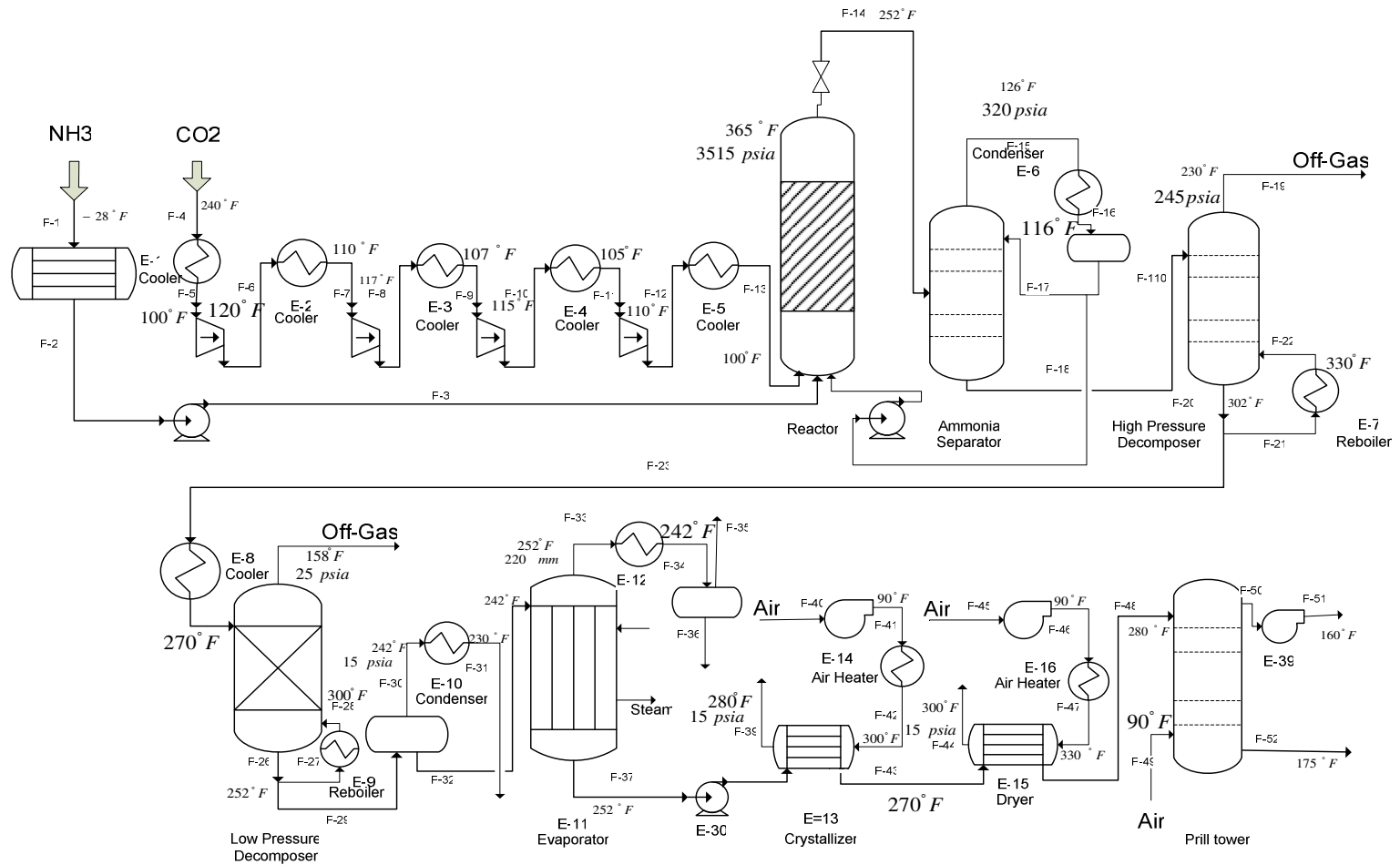


Fig. 5.1 Urea Manufacture—Partial Ammonia Recycle Process

In the reactor, ammonia and carbon dioxide are reacted to produce molten ammonium carbamate. Subsequently, decomposition of 72 % of the carbamate yields urea and water. This reaction is carried out adiabatically at 3,515 psia and the outlet temperature is $365^{\circ} F$ with residence time of 35 minutes and ratio of $\frac{NH_3}{CO_2} = 4.6$. At the top of the reactor there is a valve to reduce the pressure to 320 psia before taking the mixture to an ammonia separator. The top stream of the separator is almost pure ammonia. Part of the top of the separator goes as a reflux and the rest is recycled to the reactor. At the bottom of the separator liquid of water, ammonia, ammonium carbamate, and urea are taken to the top of a high pressure decomposer where 87% of ammonium carbamate decomposes to ammonia and carbon dioxide gases which exit at the top with some water. At the bottom of the high pressure decomposer, the liquid is cooled and fed to a low pressure decomposer where further decomposition of ammonium carbamate takes place. The stream leaving the top of the low-pressure decomposer contains ammonia, carbon dioxide, and water vapor. At the bottom of the low pressure decomposer, liquid urea and water leave with some remains of ammonium carbamate and are separated at the flash vessel. This solution is taken to an evaporator to reach a urea concentration of 90%. Then, the urea solution is pumped to a crystallizer to reach a water content less than 1% by blowing hot air counter-currently. Urea crystals are formed at the drier where water content is reduced to 0.3%. The urea crystals are elevated to the top of prill tower and melted on prill tubes by blowing air counter-currently. At the bottom, solid urea prills are transported. Part of this process is based on (Elkin 1969).

5.1.1 Data Extraction

By considering the whole process, heating and cooling duties were identified. The current network of heat exchangers is shown by Fig. 5.2. Data for the flow rate of each stream as well as supply and target temperatures were extracted. The extracted data are shown by Tables 5.1 and 5.2.

From the process data, the following are the current usages of heating and cooling utilities:

$$Q_{Original}^{HU} = 79.8 \text{ MM Btu/hr} \quad (5.1)$$

and

$$Q_{Original}^{CU} = 89.2 \text{ MM Btu/hr} \quad (5.2)$$

Taking the specific heat of the seawater to be 0.9675 Btu/lb °F, the flowrate of seawater corresponding to the various heat duties in the coolers are calculated as shown in Table 5.4 A on page 49 for hot streams and Table 5.4 B on page 50 for cold streams.

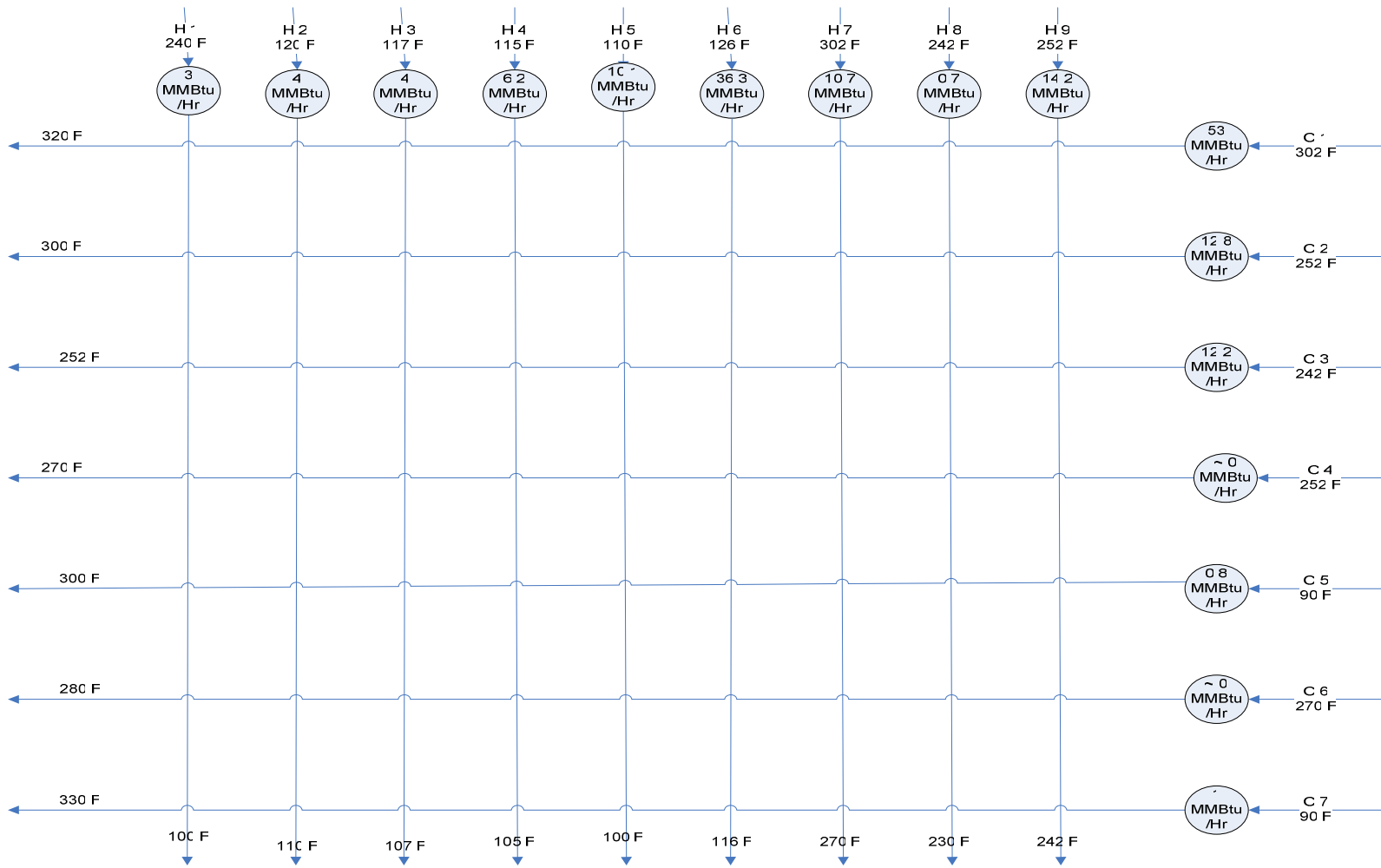


Fig. 5.2 Current Heat-Exchange Network

Table 5.1 Data for the Process Hot Streams

Heat Exchanger Hot Streams		Heat Load (MMBtu/HR)	T supply (F)	T target (F)	F*Cp MM Btu/(Hr.F)
E-1	Cooler	3	240	100	0.021
E-2	Interstage Cooler	4	120	110	0.400
E-3	Interstage Cooler	4	117	107	0.400
E-4	Interstage Cooler	6.2	115	105	0.620
E-5	After Cooler	10.1	110	100	1.010
E-6	Condenser	36.3	126	116	3.630
E-8	cooler	10.7	302	270	0.334
E-10	Condenser	0.7	242	230	0.058
E-12	Condenser	14.2	252	242	1.420
Total Current Cooling Utilities		89.2			

Table 5.2 Data for the Process Cold Streams

Heat Exchanger Cold Streams		Heat Load (MMBtu/HR)	T supply (F)	T target (F)	F*Cp MM Btu/(Hr.F)
E-7	Reboiler	53	302	320	2.944
E-9	Reboiler	12.8	252	300	0.267
E-11	Evaporator	12.2	242	252	1.220
E-13	Crystalizer	~ 0	252	270	~ 0.000
E-14	Air Heater	0.8	90	300	0.004
E-15	Dryer	~ 0	270	280	~ 0.000
E-16	Air Heater	1	90	330	0.004
Total Current Heating Utilities		79.8			

Table 5.3 Flowrate of Seawater in Process Coolers

Heat Load MM Btu/Hr	Flow rate lb/Hr
3.0	1,550,351
4.0	2,067,135
4.0	2,067,135
6.2	3,204,060
10.1	5,219,517
36.3	18,759,254
10.7	5,529,587
0.7	361,748
14.2	7,338,330
Total = 89.2	Total = 46,097,121

Therefore, the current flowrate of seawater used for cooling is 46,097,121 lb/hr or 4.038×10^{11} lb/yr. To chlorinate the seawater to a concentration of 3.0 mg/L (about 2.96 ppm weight basis), the current dosage of chlorine is 136.4 lb/hr or 1,194,864 lb/yr. The objective of this case study is to develop cost-effective strategies to reduce the discharged load of chlorine (expressed as free residual chlorine) to 10.0 lb/hr.

5.2. HEAT INTEGRATION

In order to construct a cascade diagram, we need to consider all the supply and target temperature of all process hot and cold streams. From the above supply and target temperatures, a table is constructed. A minimum temperature difference is chosen to be $18^\circ F$. The temperature interval diagram is shown in Fig. 5.3.

Next, the table of exchangeable loads is constructed to evaluate the amount of enthalpy change for each stream in each temperature interval. The results are shown in Table 5.3.

Temp. Interval	Hot Streams	T (F)	t (F)	Cold Streams
			348	330
1		338	320	
2		320	302	↑ C1
3		318	300	
4	H7 ↓	302	284	↑ C2
5		298	280	↑ C4
6		288	270	↑ C6
7		270	252	
8		260	242	↑ C2
9		252	234	↑ C3
10	H8 ↓	242	224	
11	H1 ↓	240	222	
12		230	212	
13	H6 ↓	126	108	
14	H2 ↓	120	102	
15	H3 ↓	117	99	
16		116	98	
17	H4 ↓	115	97	
18	H5 ↓	110	92	
19		108	90	
20		107	89	↑ C5
21		105	87	↑ C7
22		100	82	

Fig. 5.3 Temperature Interval Diagram

Table 5.4 A Table of Exchangeable Loads for Hot Streams (all numbers are in MM Btu/Hr)

348	Intervals	H1	H2	H3	H4	H5	H6	H7	H8	H9	Total
338	1	0.000	0	0	0	0	0	0	0	0	0.000
320	2	0.000	0	0	0	0	0	0	0	0	0.000
318	3	0.000	0	0	0	0	0	0	0	0	0.000
302	4	0.000	0	0	0	0	0	0	0	0	0.000
298	5	0.000	0	0	0	0	0	1.338	0	0	1.338
288	6	0.000	0	0	0	0	0	3.344	0	0	3.344
270	7	0.000	0	0	0	0	0	6.019	0	0	6.019
260	8	0.000	0	0	0	0	0	0	0	0	0.000
252	9	0.000	0	0	0	0	0	0	0	0	0.000
242	10	0.000	0	0	0	0	0	0	0	14.200	14.200
240	11	0.000	0	0	0	0	0	0	0.117	0	0.117
230	12	0.214	0	0	0	0	0	0	0.583	0	0.798
126	13	2.229	0	0	0	0	0	0	0	0	2.229
120	14	0.129	0	0	0	0	21.780	0	0	0	21.909
117	15	0.064	1.200	0	0	0	10.890	0	0	0	12.154
116	16	0.021	0.400	0.400	0	0	3.630	0	0	0	4.451
115	17	0.021	0.400	0.400	0	0	0	0	0	0	0.821
110	18	0.107	2.000	2.000	3.100	0	0	0	0	0	7.207
108	19	0.043	0	0.800	1.240	2.020	0	0	0	0	4.103
107	20	0.021	0	0.400	0.620	1.010	0	0	0	0	2.051
105	21	0.043	0	0	1.240	2.020	0	0	0	0	3.303
100	22	0.107	0	0	0	5.050	0	0	0	0	5.157
Total		3.000	4.000	4.000	6.200	10.100	36.300	10.700	0.700	14.200	89.200

Table 5.4 B Table of Exchangeable Loads for Cold Streams (all numbers are in MM Btu/Hr)

330	Intervals	C1	C2	C3	C4	C5	C6	C7	Total
320	1	0.000	0	0	0	0	0	0.042	0.042
302	2	53.000	0	0	0	0	0	0.075	53.075
300	3	0	0.000	0	0	0	0	0.008	0.008
284	4	0	4.267	0	0	0.061	0	0.067	4.394
280	5	0	1.067	0	0	0.015	0	0.017	1.099
270	6	0	2.667	0	0	0.038	0	0.042	2.746
252	7	0	4.800	0	0	0.069	0	0.075	4.944
242	8	0	0	12.200	0	0.038	0	0.042	12.280
234	9	0	0	0	0	0.030	0	0.033	0.064
224	10	0	0	0	0	0.038	0	0.042	0.080
222	11	0	0	0	0	0.008	0	0.008	0.016
212	12	0	0	0	0	0.038	0	0.042	0.080
108	13	0	0	0	0	0.396	0	0.433	0.830
102	14	0	0	0	0	0.023	0	0.025	0.048
99	15	0	0	0	0	0.011	0	0.013	0.024
98	16	0	0	0	0	0.004	0	0.004	0.008
97	17	0	0	0	0	0.004	0	0.004	0.008
92	18	0	0	0	0	0.019	0	0.021	0.040
90	19	0	0	0	0	0.008	0	0.008	0.016
89	20	0	0	0	0	0.000	0	0.000	0.000
87	21	0	0	0	0	0.000	0	0.000	0.000
82	22	0	0	0	0	0.000	0	0.000	0.000
Total		53.000	12.800	12.200	0.000	0.800	0.000	1.000	79.800

From Tables 5.4 A and 5.4 B, the enthalpy difference from cold and hot streams at each temperature interval is required for the cascade diagram. Each box of the cascade represents a temperature interval. The Enthalpy difference of hot streams at that interval is represented by an arrow entering that stage. On the other hand, the Enthalpy difference of cold streams for the same interval represents the cooling load required for that interval. Then, heat balance is carried out around each temperature interval and the residual heat is transferred to the next stage. This is done for all stages of the cascade diagram. The cascade diagram is shown by Fig. 5.4.

The most negative residual heat is used to determine the location of the pinch point and the minimum heating utility. The positive magnitude of the most negative residual is added to the top stage and corresponds to the minimum heating utility required. Consequently, the cascade calculations are revised as shown in Fig. 5.5. The revised residual heat from the last stage is the minimum cooling utility required for the process.

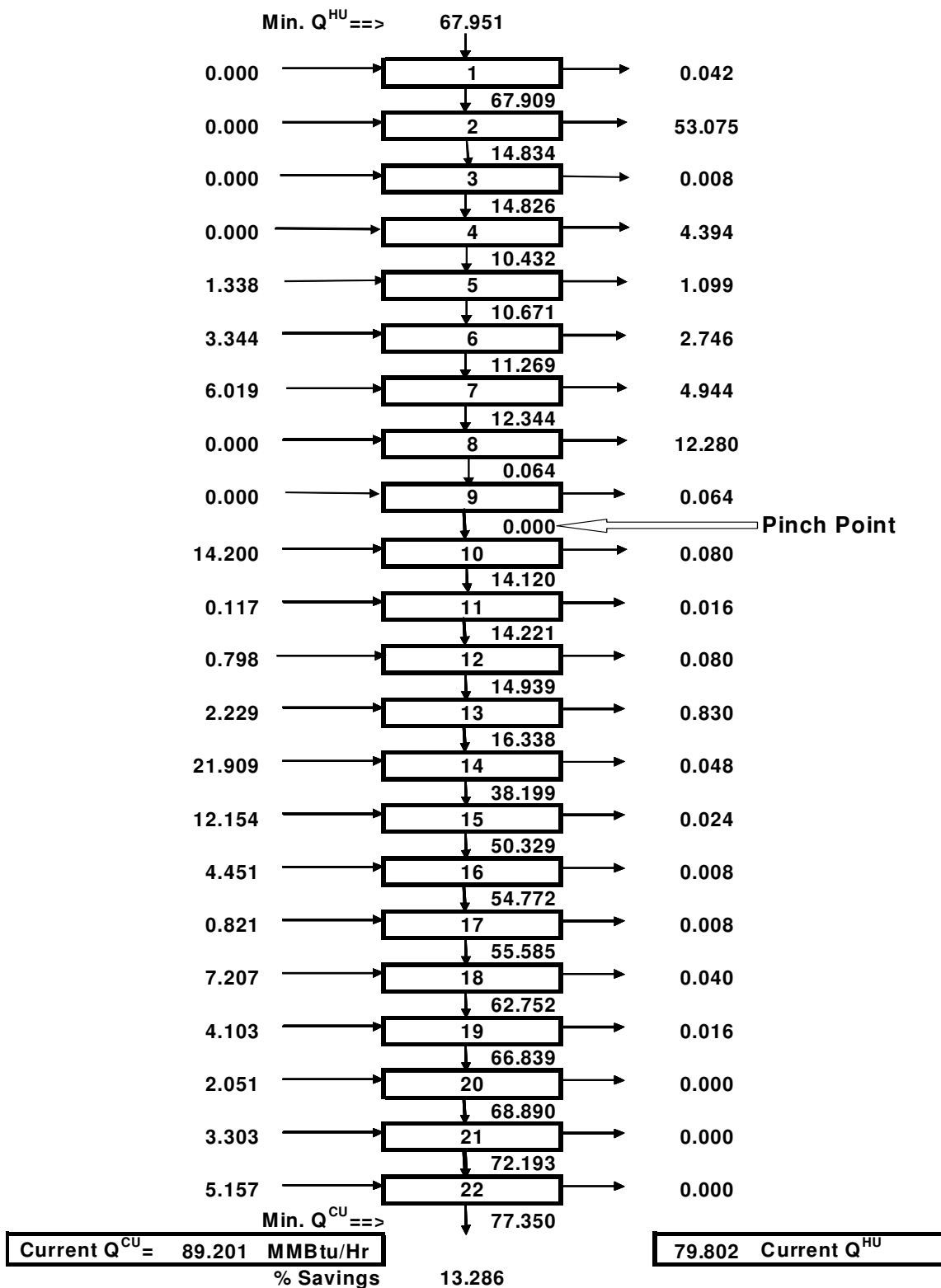


Fig. 5.4 Cascade Diagram

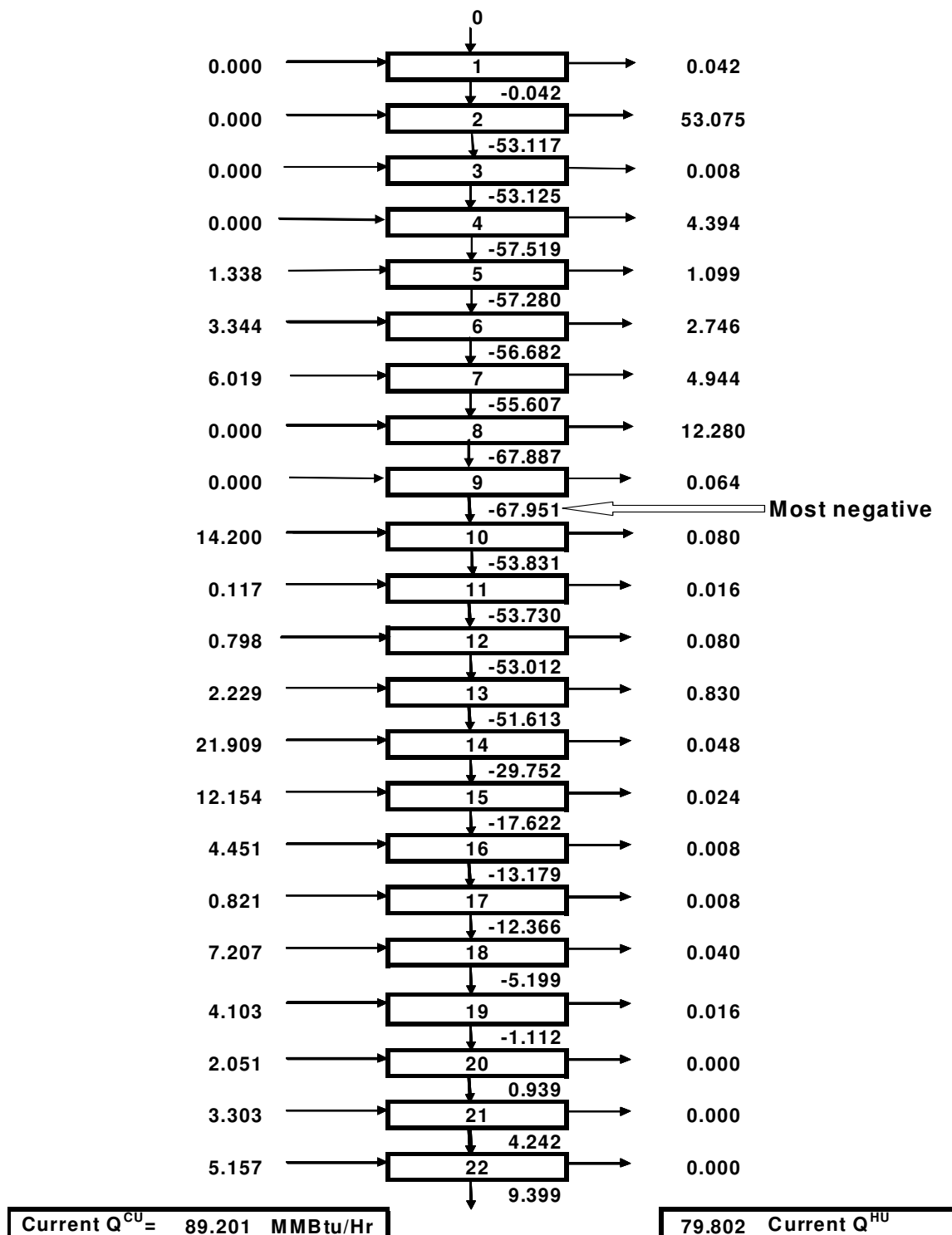


Fig. 5.5 Revised Cascade Diagram

As a result of heat integration from the cascade diagram, the target for minimum heating utilities is 67.68 MM Btu/hr and the target for minimum cooling utilities is 77.08 MM Btu/hr.

Compared with the original usage of seawater cooling utility, there is a potential of saving of 13.59% of cooling utility and the same 13.59% of heating utility. By inspection, one scheme for implementing heat integration is shown by Fig. 5.6. The grid diagram for matching the streams and showing the heat exchangers is shown in Fig. 5.7.

As mentioned in Chapter IV, any additional heat exchanger must pass the cost-benefit analysis to justify that the value of annualized saved energy over the cost of installing the new heat exchanger unit. This ratio for new exchanger should equal or exceeds the ROI return of investment of the company. The results are shown by Fig. 5.8.

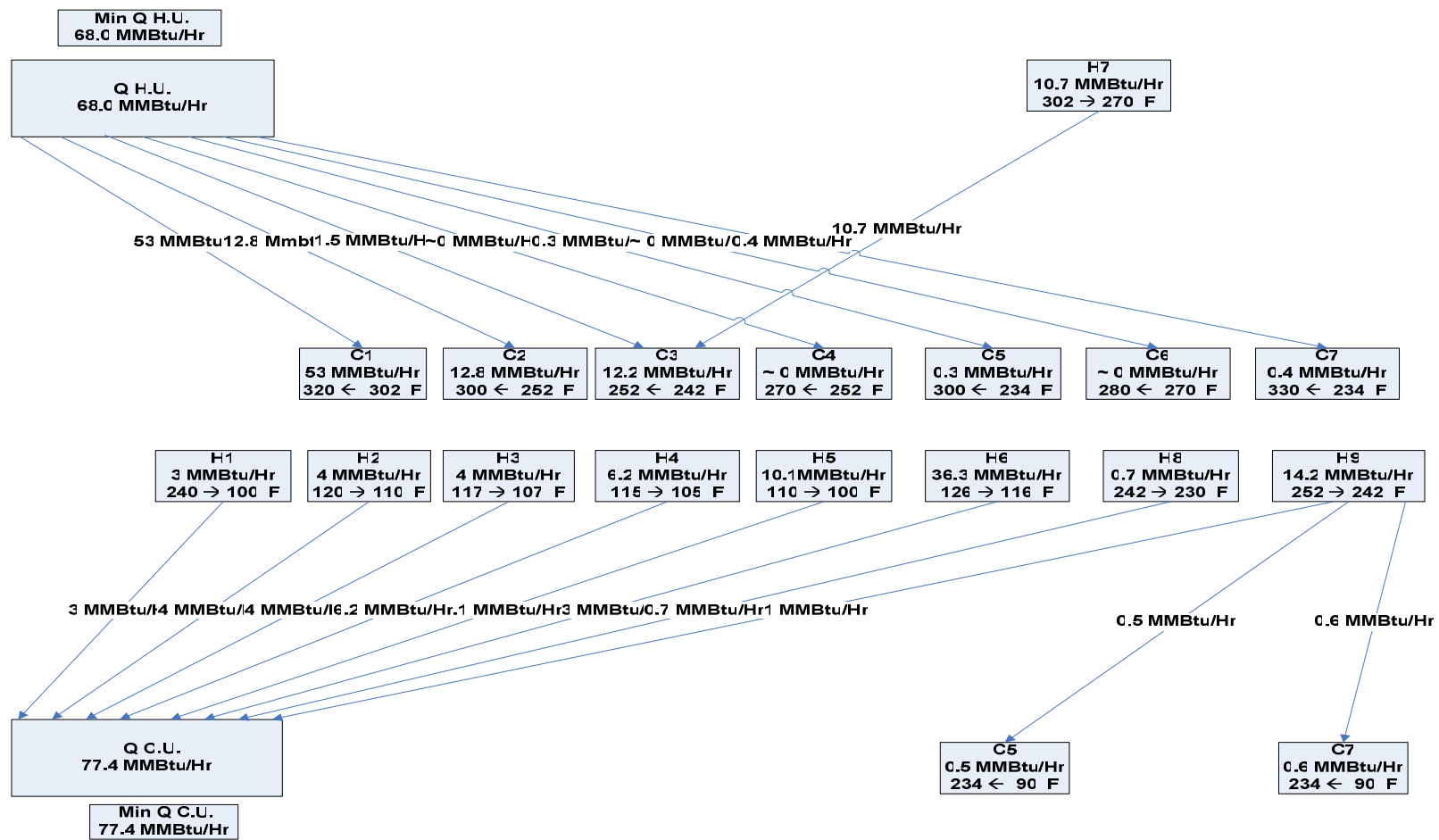


Fig. 5.6 Matching the Streams

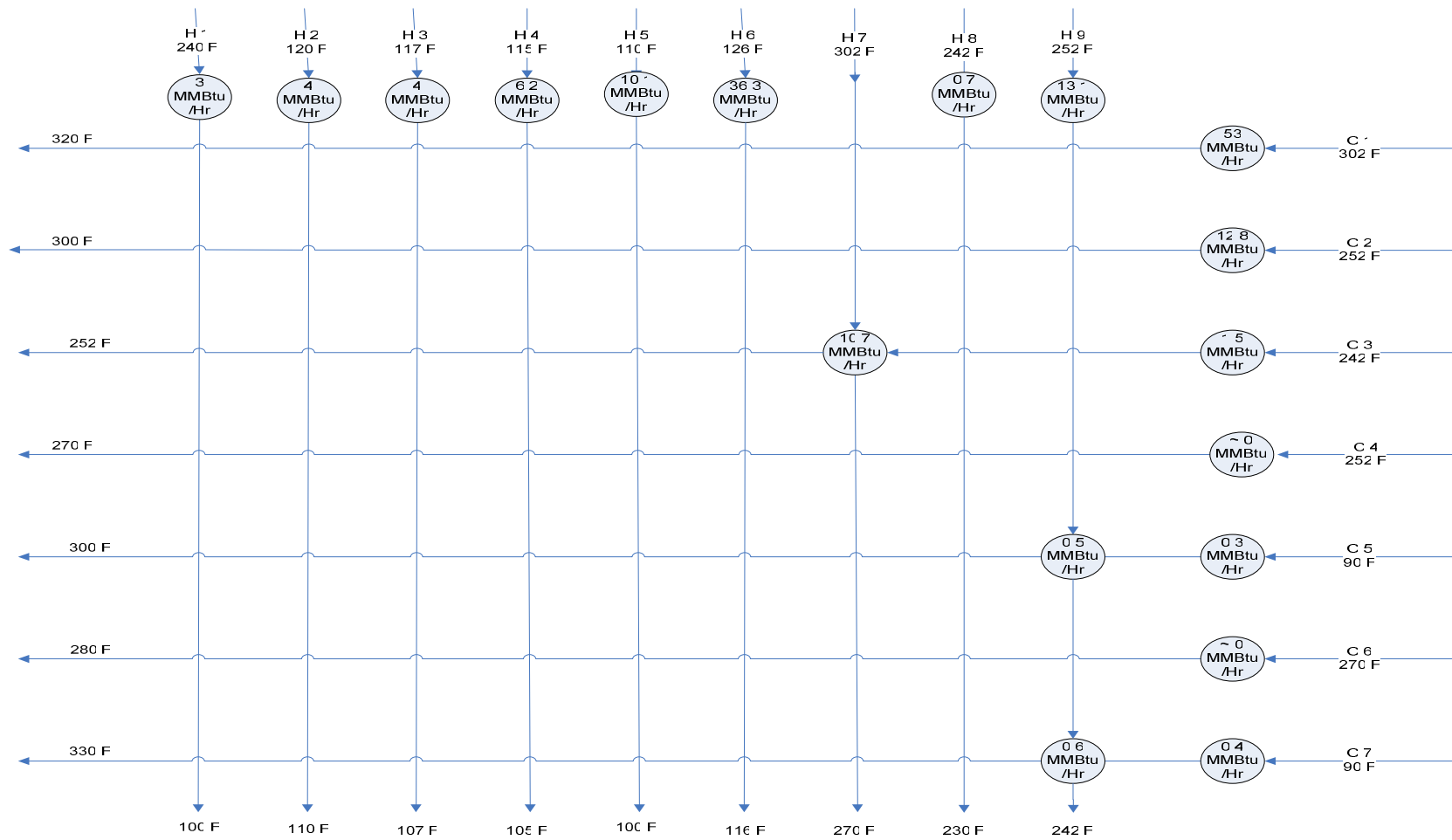


Fig. 5.7 The Grid Diagram for the Heat Exchange Network

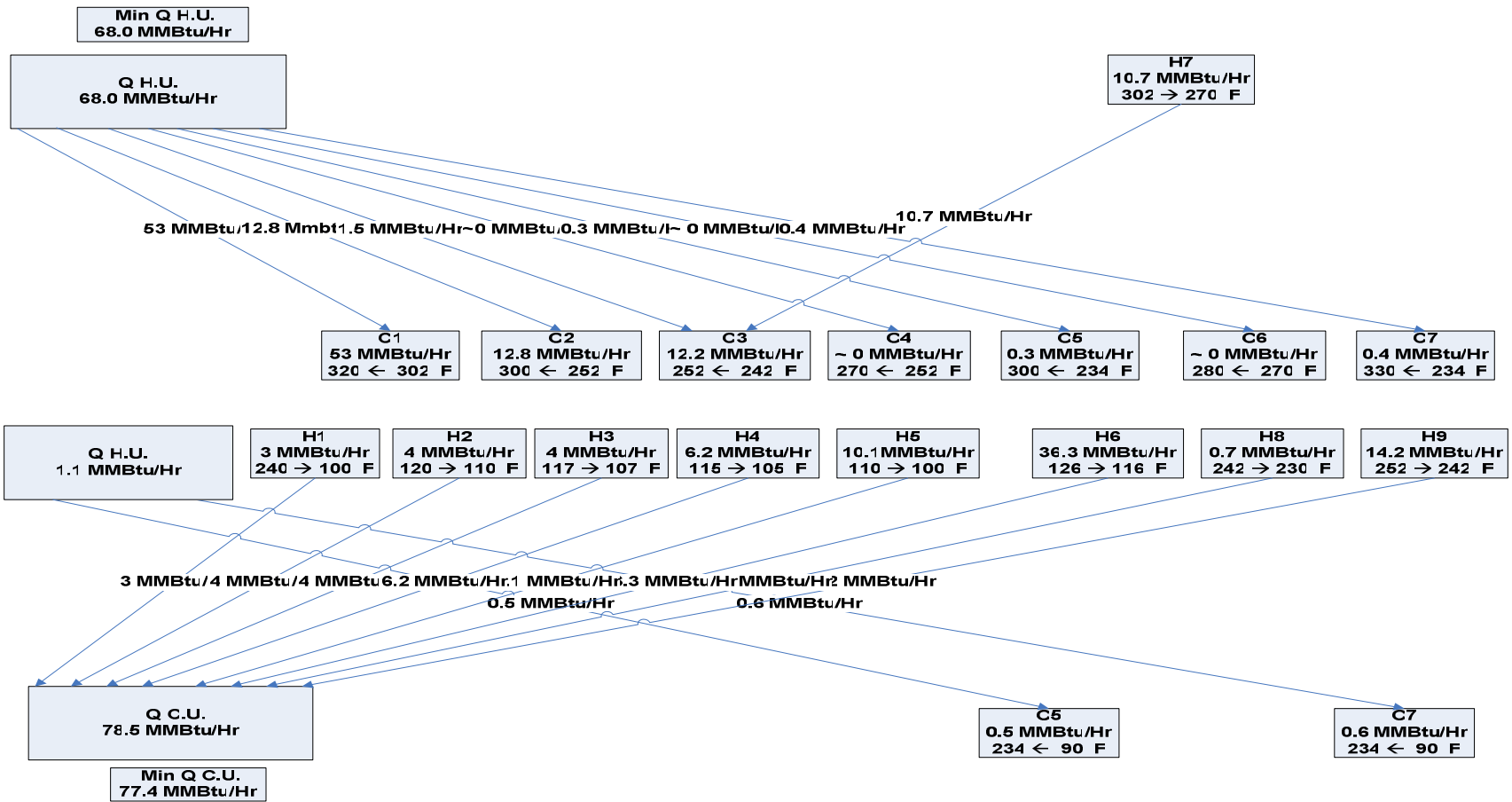


Fig. 5.8 Matching the Streams After Cost-Benefit Analysis

After conducting the cost-benefit analysis, the result is to remove one heat exchanger from the current network and to add a new heat exchanger for the integrated match. Because of the comparable heat duties and surface areas of the two exchangers, the existing exchanger can be used instead of purchasing a new exchanger. The final result is that heat integration can be implemented without the need for new heat exchangers. The result is shown by Fig. 5.9. The result is a net savings of 10.7 MM Btu/hr of heat integration.

Let us refer the heating and cooling utilities after heat integration and the cost benefit analysis as Q_{AHI}^{HU} and Q_{AHI}^{CU} , respectively.

Therefore,

$$\begin{aligned}
 Q_{AHI}^{HU} &= Q_{Current}^{HU} - Q_{Reduction}^{HU} & (5.3) \\
 &= 79.8 - 10.7 = 69.1 \text{ MM Btu/hr}
 \end{aligned}$$

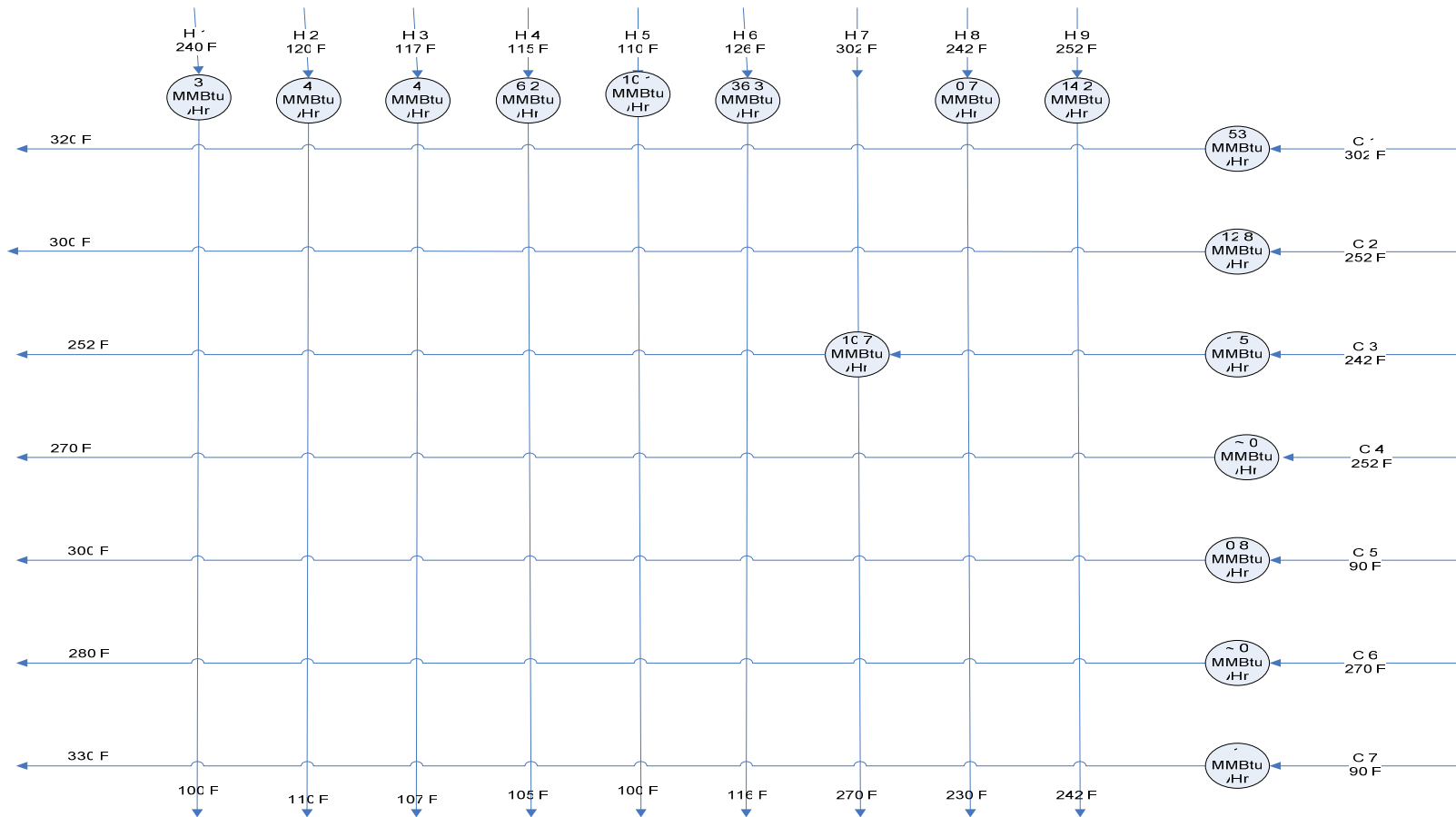


Fig. 5.9 The Modified Grid Diagram for the Heat Exchange Network

$$\begin{aligned}
 Q_{AHI}^{CU} &= Q_{Current}^{CU} - Q_{Reduction}^{CU} \\
 &= 89.2 - 10.7 = 78.5 \text{ MM Btu/hr}
 \end{aligned}
 \tag{5.4}$$

But

$$Q_{AHI}^{CU} = F_{AHI}^{S.W.} * C_P * \Delta T_{Original}^{SW}
 \tag{5.5 a}$$

or

$$F_{AHI}^{S.W.} = \frac{Q_{AHI}^{CU}}{C_P * \Delta T_{Original}^{SW}}
 \tag{5.5 b}$$

where $F_{AHI}^{S.W.}$ is the required flowrate of seawater after heat integration. Since the cooling duty has been reduced as a result of heat integration, the required flowrate of seawater after heat integration will also decrease. Indeed, the ratio of the seawater after heat integration and before heat integration is expressed as follows:

$$\frac{F_{AHI}}{F_{Original}} = \frac{Q_{AHI}^{CU}}{Q_{Original}^{CU}}
 \tag{5.6}$$

Hence,

$$F_{AHI} = (78.5/89.2) * 46,097,121 = 40,567,533 \text{ lb/hr}
 \tag{5.7}$$

Considering the cost of heating utility being \$6/MM Btu, we get

Savings in heating utility from integrated heat exchange :

$$Q_{\text{Reduction}}^{HU} * \text{Cost of } Q^{HU} = \left(\frac{10.7 \text{MMBtu}}{\text{Hr}} \right) * \left(\frac{8760 \text{Hr}}{\text{Year}} \right) * \left(\frac{6\$}{\text{MMBtu}} \right) \quad (5.8)$$

$$= \frac{\$562,392}{\text{Year}}$$

Considering the cost of cooling utility being \$7/MM Btu, we get

Savings in cooling utility from integrated heat exchange :

$$Q_{\text{Reduction}}^{CU} * \text{Cost of } Q^{CU} = \left(\frac{10.7 \text{MMBtu}}{\text{Hr}} \right) * \left(\frac{8760 \text{Hr}}{\text{Year}} \right) * \left(\frac{7\$}{\text{MMBtu}} \right) \quad (5.9)$$

$$= \frac{\$656,124}{\text{Year}}$$

Saving in chlorine dosage after heat integration :

$$\text{Fractional saving in cooling utility} * \text{Original chlorine dosage} = 0.136 * 1,194,864 \quad (5.10)$$

$$= 162,502 \text{ lb/yr}$$

There was savings in chlorine came from reduction in seawater usage from heat integration. This amount which was saved from chlorine was supposed to treat the reduction amount of seawater. Always, in order to save the biocide we need to reduced the amount of seawater needed in the cooling system.

Savings in chlorine cost from integrated heat exchange = Saving in chlorine dosage*cost of chlorine (5.11)

Considering chlorine cost to be \$0.15/lb Cl₂, we get

Savings in chlorine cost from integrated heat exchange = 162,502*0.15 = \$24,375/yr

The Net Saving for the HEN = Savings from $Q_{Reduction}^{HU}$ + Savings from $Q_{Reduction}^{CU}$

- Annualized Fixed Cost of Heat Exchangers

+ Total Chemical Savings (Chlorine Dosage) (5.12)

= \$1,242,891/yr

5.3. MAXIMIZING DISCHARGED TEMPERATURE

Next, the temperature span for the seawater is maximized. Originally,

$$\Delta T_{Original}^{SW} = 2^{\circ} C \quad (5.13)$$

Because of thermal-pollution constraint, the limit of ΔT^{SW} is subject to a maximum limit of $3^{\circ} C$. Hence,

$$\Delta T_{max}^{SW} = 3^{\circ} C \quad (5.14)$$

As a result of temperature maximization, we get flowrate of seawater after temperature maximization, F_{ATM}^{SW} , to be

$$F_{ATM}^{SW} = \frac{\Delta T_{Original}^{SW}}{\Delta T_{max}^{SW}} F_{AHI}^{SW} \quad (5.15)$$

Similarly, the chlorine dosage is decreased by the same proportion. This leads to annual savings of \$53,623 in chlorine cost as a result of maximizing the temperature span for seawater.

5.4. MINIMIZING CHLORINE DOSAGE

Next, attention is given to minimizing chlorine dosage. Consider seawater characteristics comparable to those examined by (Goldman et al. 1979), a minimum dosage of 0.24 mg chlorine per liter of seawater is used. Table 5.5 summarize the results of (Goodman 1987) for chlorine consumption. This is important in determining remaining chlorine in effluent seawater. The data of (Goldman et al. 1979) were plotted in Fig. 5.10 A for residual chlorine and Fig. 5.10 B for consumed chlorine.

Since, the data of Goldman were showing that 0.24 mg/L of chlorine is the optimal dosage, so the chlorine dosage higher than 0.24 mg/L will result with no consumption. The assumption is no or minimal consumption and those results are shown by Table 5.6. All data with * are based on the previous assumption.

Table 5.5 Chlorine Dosing Level and Consumption (Goldman et al. 1979)

Chlorine Dosing Level	Chlorine Consumed	Chlorine Discharged
(mg/L)	(mg/L)	(mg/L)
0.24	0.17	0.07
0.48	0.3	0.18
1.02	0.45	0.57

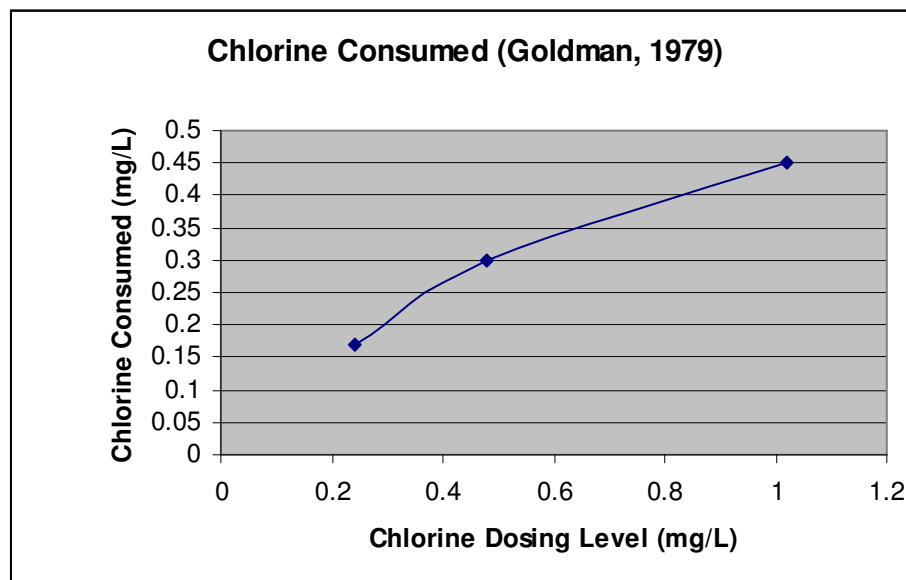


Fig. 5.10 A Chlorine Consumed (Goldman et al. 1979)

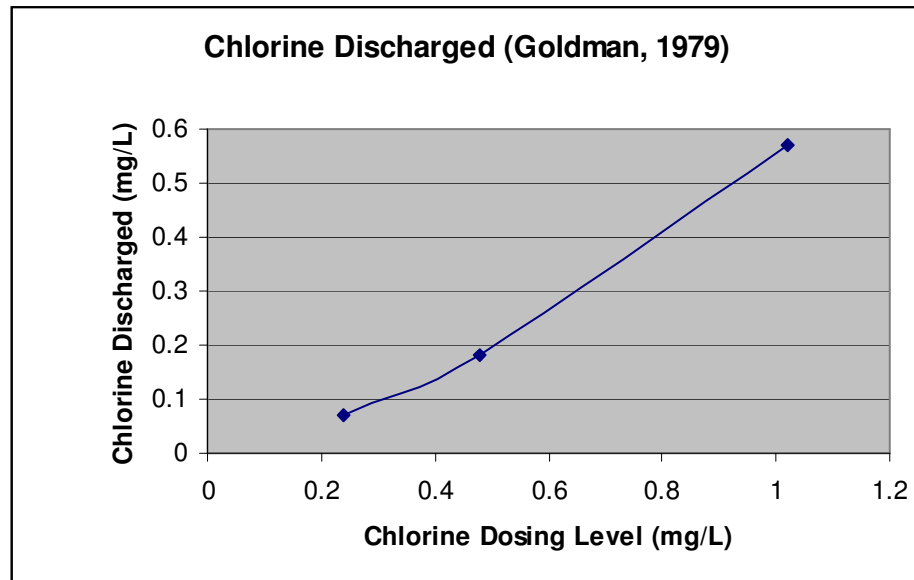


Fig. 5.10 B Chlorine Discharged (Goldman et al. 1979)

Table 5.6 Estimated Chlorine Discharge for Different Doses

Chlorine Dosing Level (mg/L)	Chlorine Residuals (Goldman,1979) (mg/L)	Chlorine Consumed (Goldman,1979) (mg/L)
0.24	0.07	0.17
0.48	0.18	0.3
1.02	0.57	0.45
1.5	1.05*	0.45*
2	1.54*	0.46*
2.5	2.04*	0.46*
3	2.53*	0.47*

The results of chlorine added and discharged for the various strategies are shown by Table 5.7.

Table 5.7 Added and Discharge Chlorine

	Chlorine Added		Chlorine Discharged	
	$D_{in}^{Cl_2}$	$L_{in}^{Cl_2}$	$D_{out}^{Cl_2}$	$L_{out}^{Cl_2}$
	(mg/L)	(lb/Hr)	(mg/L)	(lb/Hr)
Original	3	136.411	2.53	115.040
Reduction in Cooling Utilities by Heat Integration	3	120.144	2.53	101.321
Revised Discharged Temperature	3	73.601	2.53	62.070
Adjusted Chlorine Dosage	0.24	6.496	0.07	1.895

The result of these changes is that the discharged load of chlorine is 1.895 lb/hr which is much less than the required regulation of 10 lb/hr. Therefore, there is no need to add a dechlorination device at the end of the pipe. Figure 5.11 summarizes the reduction in chlorine added and discharged as a result of the various strategies.

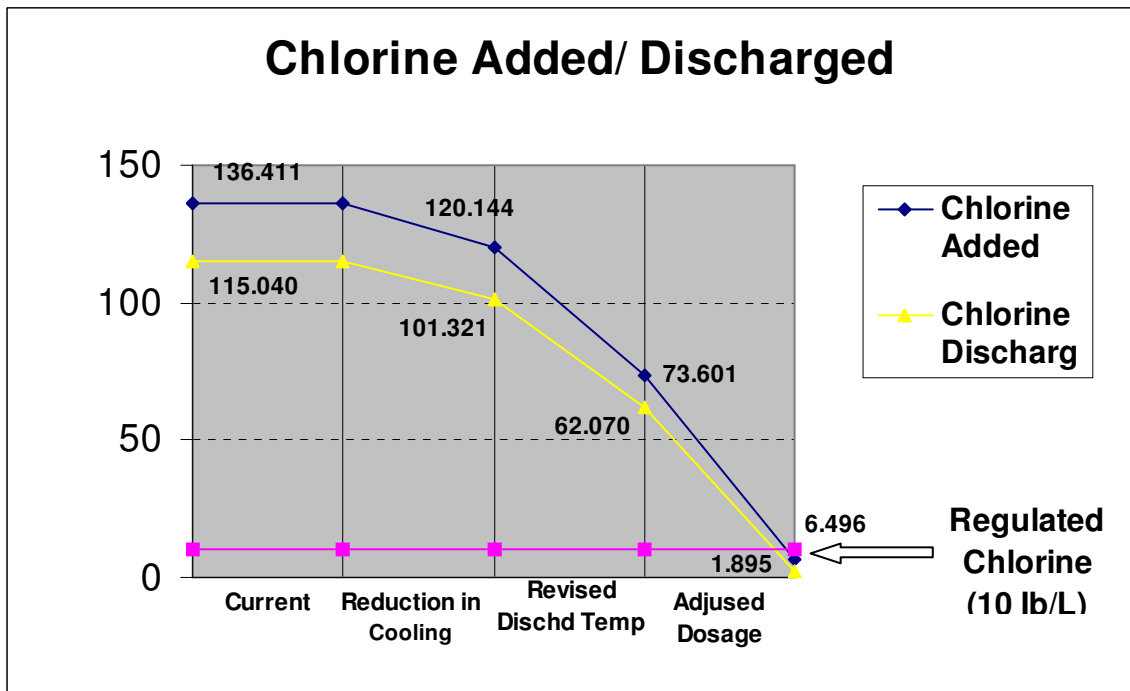


Fig. 5.11 Reduction in Chlorine Added and Discharged

Figure 5.12 is an overview of the reduction in seawater flowrate as a function of the various strategies. Additionally, Fig. 5.13 is a summary of the cost savings as a result of implementing each strategy:

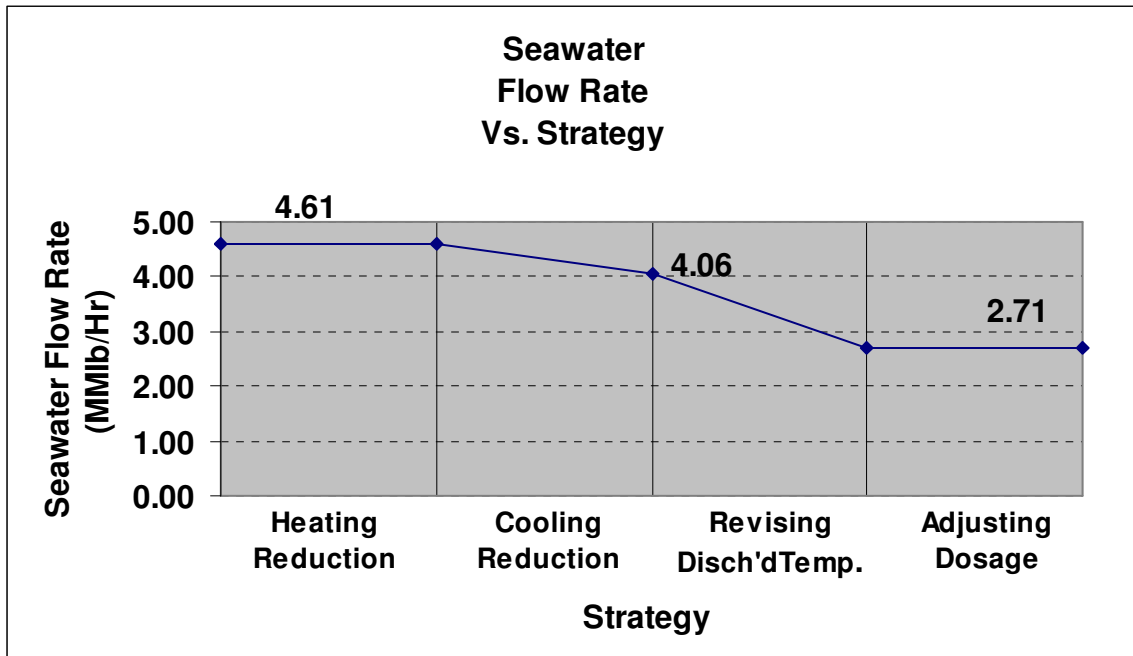


Fig. 5.12 Reduction in Seawater Flowrate

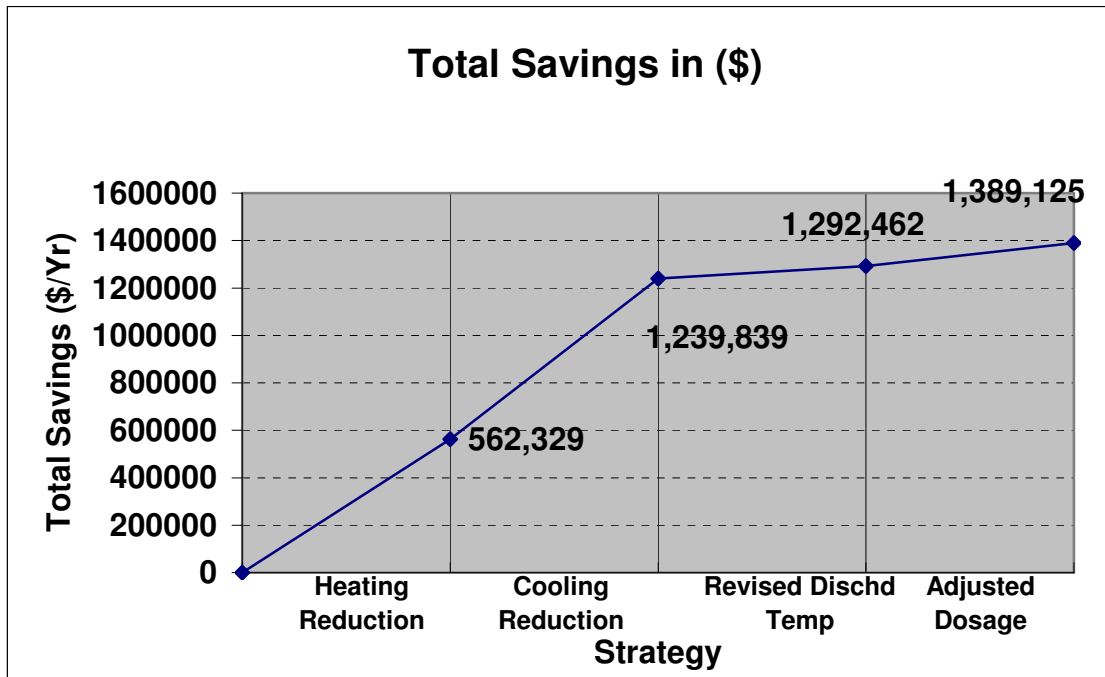


Fig. 5.13 Cost Savings Resulting From the Various Strategies

As can be seen from the results, chlorine discharge may be significantly reduced while decreasing the operating cost of the process. This is a fundamentally different approach and result from the addition of end-of-pipe treatment units that incur cost. The major savings come from the reduction in heating and cooling utilities. It is also worth noting that the savings from the reduction in biocide dosage are small compared to the savings from heating and cooling utilities. However, the reduction in chlorine usage and discharge has a major positive impact on the environment.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A new approach has been introduced for reduction in biocide usage and discharge in seawater-cooling applications. Process integration techniques have been incorporated in a hierarchical design approach that seeks to minimize cooling duties, seawater flowrate, and biocide dosage. Heat integration techniques have been used to reduce cooling utilities by synthesizing a heat-exchange network. In addition to reducing cooling duty, heating utility is also reduced as a result of heat integration. Cost-benefit analysis is carried out for the matched heat exchangers to insure economic profitability. By maximizing the temperature range for seawater within the process and by optimizing the applied load of biocide, additional savings are achieved to reduce cost and biocide discharge. A case study on urea production has been solved to illustrate the usefulness of this approach. The case study also shows that the majority of cost savings come from heat integration. Finally, the case study indicates that it is possible to go below the environmental limits on biocide discharge while achieving more cost savings.

The following research activities are recommended for future work:

1. Mass-Integration for process modifications (in addition to heat integration).
2. Simultaneous mass and heat integration to make changes in the processing scheme in conjunction with optimizing the utility system.

3. Development of detailed seawater chemistry and biocide usage and discharge models.
4. Dynamic modeling of chlorine injection and propagation system. This is particularly important in modeling and optimizing pulse and shock dosage. Because of the simultaneous algebraic-differential equations resulting from this model, a tailored global optimization technique must be developed to help minimize the biocide dosage while satisfying process requirements and meeting environmental regulations.
5. Alternative routing of discharged seawater (e.g. to desalination plants).
6. Simultaneous consideration of seawater cooling system with process water system.

REFERENCES

- El-Halwagi MM (1997) Pollution prevention through process integration. Systematic Design Tools
- El-Halwagi MM, Srinivas BK & Dunn RF (1995) Synthesis of optimal heat-induced separation networks. Chemical Engineering Science 50: 81-97
- Elkin LM (1969) Urea. Process Economics Program pp 111-127). Stanford Research Institute, Menlo Park, California
- Goldman JC, Wuimby HL & Capuzzo JM (1979). Water Research 13: 315
- Goodman PD (1987) Effect of chlorine on materials for sea water cooling systems: A review of chemical reactions. British Corrosion Journal 22: 56-62
- Grant DM & Bott TR (2003) Biocide dosing strategies for biofil control. Conference on Heat Exchanger Fouling and Cleaning: Fundamentals and Applications. Santa Fe, New Mexico
- Hass CN & ASCE M General kinetics of disinfection processes. Philadelphia
- Hom LW (1972) Kinetics of Chlorine Disinfection of an Ecosystem. Journal of the Sanitary Engineering Division 98: 138-194
- Lambert RJW & Johnston MD (2000) Disinfection Kinetics: a new hypothesis and model for the tailing of log-survivor/time curves. Journal of Applied Microbiology 88: 907-913
- Langford T (1977) Environmental management of coastal cooling discharges in Hong kong. Chemistry & Industry: 612-616
- Linnhoff B & Hindmarsh E (1983) The pinch design method for heat exchanger networks. Chemical Engineering Science 38: 745-763
- Ma SWY, Kueh CSW, Chiu GWL, Wild SR & Yip JY (1998) Environmental management of coastal cooling water discharges in hong kong. Water Science and Technology 38: 267-274
- Oldfield JW & Todd B (1981) Corrosion problems caused by bromine formation in MSF desalination plants. Desalination 38: 233-245

Shenoy UV (1995) Heat exchange network synthesis: Process optimization by energy and resource analysis. Gulf Publ. Co., Houston, Texas:

Yang L, Chang W-S & Lo Huang M-N (2000) Natural disinfection of wastewater in marine outfall fields. *Water Research* 34: 743-750

Yukselen MA, Calli B, Gokyay O & Saatci A (2003) Inactivation of coliform bacteria in Black Sea waters due to solar radiation. *Environment International* 29: 45-50

VITA

Abdullah S. Bin-MAhfouz , was born on July 14, 1968 in Makkah, Saudi Arabia and grew up in Abha, Saudi Arabia. He has four brothers and five sisters, and he is the third eldest. Abdullah is blessed with two daughters Mariam who is ten-years old and is in fifth grade and Dhoha who is seven-years old and is in second grade. Abdullah graduated from King Fahd University of Petroleum & Minerals in 1991 with a Bachelor of Science in Applied Chemical Engineering. Then, he joined Saudi ARAMCO Oil Company based in Dhahran, Saudi Arabia from 1991 until 1994. Abdullah later joined a family business, Al-Salmiah Group, operating in two fields jewelry and auto maintenance. Then, he went back to school and joined Indiana University of Pennsylvania in Indiana (IUP), Pennsylvania in 2001 for a Master in Business Administration and graduated in 2003 with an MBA degree from IUP. In the Fall of 2003, Abdullah joined the Department of Chemical Engineering at Texas A&M University to pursue a Master of Science. He has been working under the supervision of Dr. Mahmoud El-Halwagi in the area of process integration and environmental analysis.

Abdullah's contact address: Texas A&M University, Artie McFerrin Department of Chemical Engineering, College Station, TX 77843-3122. His email address is: Abdullah005@hotmail.com or asb@tamu.edu.