

WASTE WATER MINIMIZATION USING  
PINCH ANALYSIS

A THESIS SUBMITTED IN PARTIAL FULFILMENT  
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## CERTIFICATE

This is to certify that the thesis entitled, “**Waste water minimization using Pinch Analysis**” submitted by **Ipsita Swain** in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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## ABSTRACT

This thesis lays out the basic principles for analyzing a water using operation and then compares the freshwater and wastewater flowrates for the system with and without reuse. First, the system is defined as a mass transfer problem in which the contaminant is transferred from a contaminant rich process stream to a water stream. Next, the system is analyzed treating each water-using operation separately. Finally, the minimum freshwater requirement for the integrated system is determined by maximum water reuse subject to constraints such as minimum driving force for mass transfer. For this analysis, *the concentration composite curve, the concentration interval diagram and the freshwater pinch* are introduced. The methods of regeneration reuse and recycle are also discussed. The approach for single contaminant problem is extended to multiple contaminants problem with multiple constraints. The preliminary mass exchange network is designed on the basis of concentration interval diagram and further simplification is achieved by loop breaking. The basic concepts of each method are formulated into a mathematical code to obtain computer-aided solution to a problem.

Two industrial case studies are discussed to illustrate the significance of wastewater minimization and the results obtained are compared with that predicted using analytical method. The first one is a SO<sub>2</sub> extraction problem from four process streams and the second is a petroleum refinery complex problem. An average reduction of about 20% in the freshwater requirement is achieved with water reuse while a reduction of about 60 % is achieved by regeneration reuse. There is also a reduction in the number of units in the mass exchange network by four units with water reuse.

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## NOMENCLATURE

$C_{i,in,lim}$	contaminant level in the inlet streams, ppm
$C_{i,out,lim}$	contaminant level in the outlet stream, ppm
$\Delta m_{i,tot}$	total mass load of contaminant to be transferred, kg/hr
$f_{i,lim}$	limiting water flowrate for operation i, te/hr
$C_{i,w,supply}$	contaminant concentration of the freshwater supply, ppm
$C_{i,w,out}$	contaminant concentration of the water stream leaving operation i
$f_{min}$	minimum freshwater flowrate required, te/hr
$C_{pinch}$	concentration at the pinch, ppm
$C_{regen}$	regeneration concentration, ppm
$C_0$	regeneration outlet concentration, ppm
$\Delta m_{regen}$	mass load of contaminant transferred to the freshwater stream prior to regeneration, kg/hr
$\Delta m_{pinch}$	mass load of contaminant transferred to the regenerated water stream between regeneration outlet concentration $C_0$ and the freshwater pinch, $C_{pinch}$ , ppm
$f_{regen}$	flowrate of regenerated water, te/hr
$f_{recycle}$	flowrate of recycled water, te/hr
$C_{out}$	average outlet concentration of the water supply, ppm

# Chapter 1

## INTRODUCTION

With increasing population and decreasing water resources, a lot of focus has now shifted towards conservation of water both in domestic as well as industrial processes. The process industries, which includes chemicals, petrochemicals, petroleum refining, pharmaceuticals, pulp and papers and certain food and consumer products, represents a major portion of the world economy, with their annual productions exceeding \$5 trillion. These industries use a huge quantity of water in their various processes and as a result generate a lot of wastewater. The generation of such vast quantities of wastewater demands that methods be developed to minimize the freshwater requirements of these processes for the optimization of the process industries (Mann and Liu, 1999).

Moreover, the increasing cost of freshwater and the treatment of wastewater compels the process plants to focus on the minimization of freshwater consumption. A direct consequence of this step is a reduction in generation of effluent and reduced treatment costs. Hence, the systematic approach to design of water recovery network has become a topic of interest in the field of research in the past few years.

### 1.1 Definition of the problem

The synthesis of a water recovery network can be stated as:

*Given a set of water-using processes, it is desired to determine a network of interconnections of water streams among the water-using processes so that the overall fresh water consumption is minimised while the processes receive water of adequate quality. (Savelski et al.,2000)*

In the present work the water network is proposed for extraction of SO<sub>2</sub> using water and a petroleum refinery complex consisting of a steam stripper, a hydrodesulphurization unit and a desalter.

One of the most practical tools that has been developed for the design of water recovery networks in the past 20 years is *pinch analysis*, which is used to improve the efficient use of water resources in process industries

## **1.2 What is pinch analysis?**

Pinch analysis is a rigorous, structured approach that may be used to tackle a wide range of problems related to process and site utility. This includes opportunities such as reducing costs, improving efficiency, and reducing and planning capital investment. [2]

The success of pinch technology is due the underlying simple basic concepts. This technique analyses a commodity on the basis of both quality as well as quantity, such as energy (energy pinch), water (water pinch) and hydrogen (hydrogen pinch), because cost of a process is a function of both. In general, we use high value utilities in our processes and reject waste at a lower value. For example, if we consider energy, we burn expensive natural gas to provide the process with high temperature heat, and are rejecting heat at low temperatures to air or cooling water. In the case of water, we feed pure water to processes and reject contaminated wastewater to treatment plants. For process gases, such as hydrogen, the high value utility is the pure gas which is produced on site or imported.

In all cases, the basic approach to designing the network is the ability to match individual demand for a commodity with a suitable supply. The suitability of the match depends on the quality required and the quality offered. In the case of water pinch, the commodity is water with the quality measured as purity. By maximizing the match between demand and supply, we minimize the import of utilities.

The water pinch technology is a type of mass exchange integration involving water using operations. The two main approaches used for the design of a water recovery network are the graphical approach and the mathematical programming approach. The former technique uses graphical analysis for setting targets and designing of the network. The latter involves development of mathematical codes for dealing with more complex systems, such as multiple contaminant problems.

### **1.3 Objectives of the present work**

The present work is basically divided into four parts:

1. *Analysis of the problem*: this involves studying the requirements of the problem, setting targets, identifying the minimum freshwater consumption and wastewater generation in the water using operations.
2. *Design of the network*: this involves designing a water using network that achieves the identified flowrate targets for freshwater and wastewater through water reuse, regeneration and recycle.
3. *Optimization of the network*: this involves simplifying the designed network to reduce the number of mass exchange units and to make the process economically viable. This is achieved by loop breaking techniques.
4. *Comparison of result with published work*: the results obtained from the above analysis are compared with the published work to determine their validity and significance.

### **1.4 Layout of the thesis**

In this work, water using operation is analyzed and then the freshwater and wastewater flowrates for systems without and with water reuse are compared. The concepts of regeneration and recycle are introduced for the further reduction of freshwater requirements. The methodology is developed for a single contaminant problem and then extended to more complex processes dealing with multiple contaminant problems. The concepts are then formulated into a mathematical code to obtain a computer aided solution to the problem. Finally we determine the significance of the technique by applying it to two industrial case studies: one involving extraction of SO<sub>2</sub> gas from a process stream using water as an extracting agent and the other is a petroleum refinery complex problem dealing with multiple contaminants.

## Chapter 2

### LITERATURE REVIEW

Pinch technology was initially used for the process of heat integration for the design of heat exchange networks to transfer energy from a set of hot streams to a set of cold process streams. A major breakthrough in this field was the identification of the pinch point temperature (Linnhoff and Flower, 1978; Umeda et al, 1976). Linnhoff et al. (1982) have applied the principles of thermodynamics and energy balance to systematically analyze heat flow across various temperature levels in a process. In this way, a temperature level, called the pinch point can be identified. The use of utilities is subject to certain constraints. Firstly, no heat is transferred across the pinch. Secondly, heat is added only above the pinch and lastly, cooling is done only below the pinch. In other words, hot process streams can be cooled more cost effectively above the pinch temperature by cold process streams as compared to cooling utility streams. Similarly, cold process streams can be heated below this point more effectively by using hot process streams than by using hot utility streams.

Linnhoff (1993) has illustrated the use of pinch technology to calculate energy “targets,” such as the minimum hot and cold utilities required. A sample composite curve to illustrate the process is shown in Fig 2.1. This ‘shortcut’ approach can help in choosing the best alternative before designing the network. The pinch analysis methodology to achieve the maximum heat recovery target assumes that no individual heat exchanger should have a  $\Delta T$  smaller than  $\Delta T_{min}$ . Once this assumption has been made, the Actual performance (A) will only meet the Targets (T) if there is no heat transfer across the pinch (XP). (Querzoli et al., 2003)

$\Delta T_{min}$  is defined as the  $\Delta T$  between the hot and cold composite curves at the pinch point. It is a key design parameter in deciding the trade off between capital and energy costs. A heat exchange network (HEN) with a smaller  $\Delta T_{min}$  will require greater exchanger area to compensate for less temperature driving force, and this results in higher capital cost. But this is compensated by lower energy costs due to improved heat

recovery and decreased hot and cold utility requirements. . The HEN capital cost can be calculated by using the cost of capital as the discount rate. The capital and energy costs can then be added to calculate the total cost of the HEN. (Querzoli et al., 2003)

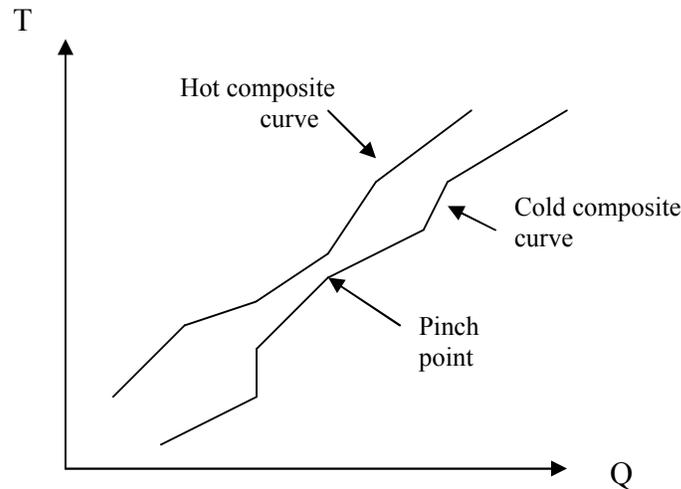


Figure 2.1 Composite Curve to determine pinch point temperature

The approach used in application of pinch technology to heat integration can be extended to mass integration. A mass exchange integration problem involves transferring mass from rich process streams (decreasing their concentrations) to lean process streams (increasing their concentrations) so that each stream reaches its desired concentration while minimizing waste production and utility consumption (including freshwater and mass separating agents) (Mann and Liu, 1999).

Takama et al. (1980) first addressed the problem of optimization water use in a petroleum refinery. The approach was to first generate a superstructure of all possible re-use and regeneration possibilities. The superstructure was then optimized by removing the less economic features of the design. El-Halwagi and Manousiouthakis (1989) addressed the more general problem of mass exchange between (MEN) a set of rich process streams and a set of lean streams. Their approach was adapted from the methodology developed for heat exchanger networks by Linnhoff and Hindmarsh (1983). El-Halwagi and Manousiouthakis (1989) defined a minimum allowable concentration difference which applied throughout the mass exchange network. Also, the method only

applied to a single key component. Later, El-Halwagi and Manousiouthakis (1990) automated the approach and introduced the concept of regeneration. In the first stage of their automated approach, a linear programming (LP) problem was formulated using thermodynamic constraints, whose solution determined the minimum cost and pinch points that limit the mass exchange between rich and lean streams. Then in the second stage a mixed integer linear program (MILP) transshipment problem was solved to identify the minimum number of mass exchange units. El-Halwagi et al. (1992) later applied this approach to the specific problem of phenol treatment in petroleum refinery wastewaters (Wang and Smith, 1994). They have provided graphical techniques such as segregation, recycle, interception and unit manipulation for mass integration. They have also studied the application of heat induced separation networks in recovery of VOCs and modeling and design of membrane systems.

Based on the similar pattern as in heat integration El-Halwagi and Manousiouthakis (1989) showed how mass transfer composite curves could be plotted using a minimum composition difference,  $\varepsilon$  (analogous to  $\Delta T_{min}$  in HENS). The mass transfer pinch can be located using this plot and the targets for the minimum flow rate of lean stream i.e. mass separating agent (MSA) can be determined. A sample composite curve is presented in Fig. 2.2 to illustrate the method. The HENS pinch design method was then adopted to design networks to achieve these targets. This method divides the problem at the pinch and does not transfer mass across it. This is sufficient to ensure the minimum MSA cost.

However, unlike HENS, there was no way of targeting the minimum capital cost for the network. This is because the driving forces for mass transfer are more complex than those for heat transfer. In HENS, the driving forces are merely the temperature differences and are clearly shown on the composite curves. However, in MENS, the driving forces involve the equilibrium relations as well and these must also be represented. (Hallale *et al.*, 2000)

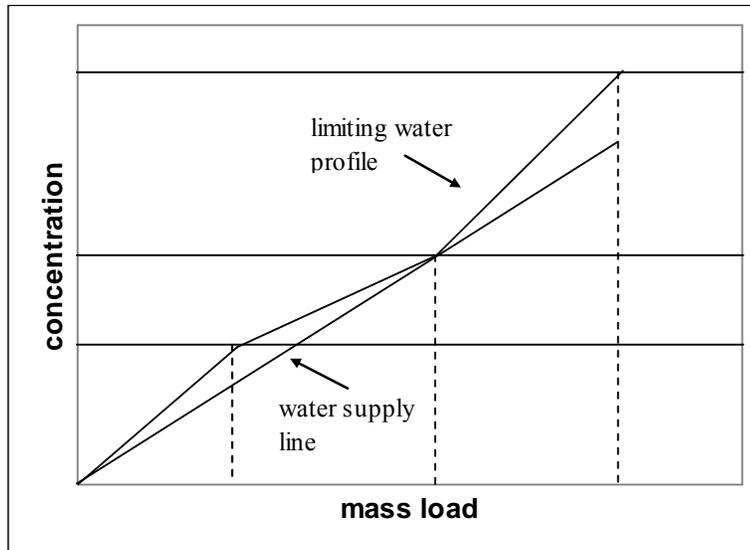


Fig 2.2 Composite curve to determine freshwater pinch concentration

El-Halwagi and Manousiouthakis (1989) recommended using the minimum number of units in the design of the network to minimize the capital costs (the minimum number of units targets is simply one less than the total number of streams). However, the size of the exchanger is also a constraint. HENS also faced a similar problem. Heat exchanger networks could be designed for minimum energy usage, but satisfactory capital costs could not be achieved. Designs focused on the minimum number of units in an attempt to minimize capital costs. Later, the targets for surface area were introduced to minimize capital cost. Hence, optimization of the total annual cost (TAC) for MENS was not straightforward.

El-Halwagi and Manousiouthakis (1989) showed how mass-load loops in an evolved design of the network could be simplified, in order to improve the total cost. This evolutionary approach depends on the initial network structure and is unlikely to give a true optimum. No amount of evolution will reach the optimum design if its topology is different from that of the initial network. This is termed a 'topology trap'.

They also showed that the minimum composition difference,  $\epsilon$ , is a parameter which can be used to optimize the network. As  $\epsilon$  approaches zero, infinitely large

exchangers will be required and thus the capital cost of the network will also be infinite. The MSA costs increases on increasing the value of  $\epsilon$ , but the capital cost decreases. There will therefore be an optimum value of  $\epsilon$  at which the TAC of the network is minimized. This is analogous to the capital/energy trade-off in HENS. Unfortunately, unlike HENS, the trade-off could not be determined before design using supertargeting. This is because capital cost targets did not exist. There was no way of determining the capital costs until the network was designed and so the optimization could only be done by carrying out many repeated designs. The absence of a capital cost target also meant that there was no guarantee that the capital cost of a network was the minimum attainable for a specific value of  $\epsilon$ . (Hallale *et al.* , 2000)

El-Halwagi and Manousiouthakis (1989) later presented an automated synthesis procedure. This procedure first determined the pinch points and minimum utility targets using linear programming. All possible networks having minimum number of units was then synthesized using mixed integer linear programming minimum. The cost of the final networks was calculated and the one with the lowest cost was selected. This was carried out iteratively for a range of  $\epsilon$  values to minimize the annualized total cost of the network. A vector of stream-dependent  $\epsilon$  values could also be used if necessary.

Papalexandri *et al.* (1994) pointed out that the main drawback of this procedure is its sequential approach. As the capital and operating costs are not considered simultaneously, the determination of optimum trade-off between them may not be possible. They applied mixed integer nonlinear programming (MINLP) to the MENS problem. Their approach was to minimize the TAC by optimizing a network hyperstructure containing many mass exchange alternatives without using pinch division.

Bagajewicz *et al.* (1998) presented state-space approach for heat and/or mass exchange network synthesis to overcome some of the limitations of the MINLP approach. This approach is analogous to process control systems and is based on the notion that the behaviour of any system can be characterized by a set of input variables, a set of output variables and input-output relations. The representation for a heat/mass exchange

network is characterized by two operators: a distribution network where stream mixing and splitting occurs and a process operator where heat or mass transfer takes place. This approach was used to tackle the problem of minimizing the TAC of heat or mass exchange networks and it was claimed that it guarantees a global optimum.

Wang and Smith (1994) applied the water pinch technique on the more generalised problem of mass exchange network synthesis (MENS). The basic concept underlying their approach was the treatment of water using operation as mass exchange problems. They introduced the concept of limiting water profiles, concentration composite curve and concentration interval diagram to determine the freshwater pinch concentration. The graphical approach was then used to calculate the minimum freshwater flowrate of a system. The methods of regeneration reuse and regeneration recycle were also included. They extended the approach of single contaminant problem to multiple contaminant problems with multiple constraints by incorporating inlet and outlet concentration shifts. They concluded that the optimum regeneration concentration was the freshwater pinch concentration.

Wang and Smith (1994) proposed the concentration interval method for the design of mass exchange networks. The limiting concentration composite curve can be used to determine the mass load in each interval for the preliminary design of the network. This network can be simplified by the process of loop breaking by the shifting of mass loads from one interval to the other. Two simple design methods have been proposed by them. The first method maximizes the use of the available concentration driving forces in individual processes. The second method allows the minimum number of water sources to be used for individual processes via bypassing and mixing.

The mass transfer model-based approach in analyzing the water using network might not be always adequate. Many operations in the process industry, such as boiler blow down, cooling tower make-up and reactor effluent are typical examples where the quantity of water used is more important than the water quality. The mass transfer-based approach fails to model these operations. Dhole *et al.* (1996) later corrected the targeting

approach by introducing new water source and demand composite curves. They also showed the fresh water consumption could be further reduced by proper mixing and bypassing.

Hallale *et al.* ((2000) showed that the water source and demand composite curves may not give a clear picture of the analysis. The targets obtained may not be a true solution, as they greatly depend on the mixing patterns (which is suppose to be a part of the network design) of the process streams. In turn, a water surplus diagram is presented (Hallale, 2002) for the targeting of minimum fresh water consumption and wastewater generation in a water recovery network. This is till date the most appropriate targeting technique in locating the utility in a water recovery network. It overcomes the limitations of the mass transfer-based approach and yet, this new representation does automatically build in all mixing possibilities to determine the true pinch point and reuse target.

However, the use of water surplus diagram involves tedious graphical drawing in locating the minimum water target of the network. Apart from the inaccuracy problem associated with the normal graphical approach, the major limitation of the water surplus diagram is that, the diagram is generated based on an assumed fresh water value. Often, this water surplus diagram has to be drawn for a few times, before the correct fresh water flowrate is finally located. Tan *et al.* (2002) lately introduced a tabular-based numerical approach called the *water cascade table* (WCT) to overcome the limitations associated with the graphical water surplus diagram (Foo *et al.*, 2006)

In this work the concept of water reuse, regeneration reuse and regeneration recycle have been discussed to determine the minimum freshwater requirement for a water using system. The approach to solving single contaminant problems has been extended to multiple contaminant problems. The basic concepts are formulated into a mathematical code to get computer aided solution to a given problem. Two industrial case studies have been analysed to illustrate the significance of the methods discussed.

### PROBLEM STATEMENT

#### 3.1 Extraction of SO<sub>2</sub>

This problem is presented to illustrate the analysis of single contaminant problems. SO<sub>2</sub> is removed from a set of four process gas streams using fresh water as a mass separating agent. Water is used in the tray column to absorb SO<sub>2</sub>. Each gas stream consists of mainly air and small amount of other gases. These gases are not absorbed in water. Stream data for this process is shown in Table 3.1.

Table 3.1: Stream data for the SO<sub>2</sub> extraction problem

Gas stream	G (kmol/hr)	Y <sub>s</sub> (kmol SO <sub>2</sub> /kmol gas)	Y <sub>t</sub> (kmol SO <sub>2</sub> /kmol gas)
1	50	0.01	0.004
2	60	0.01	0.005
3	40	0.02	0.005
4	30	0.02	0.015

The equilibrium relation for the system is given by:

$$Y = mX + b \tag{3.1}$$

where  $m = 26.1$  and  $b = -0.00326$

The limiting concentrations of SO<sub>2</sub> gas in the water stream in kmol SO<sub>2</sub>/kmol H<sub>2</sub>O for each operation are given by:

$$X_{\max, in} = \frac{Y_t - b}{m} - \epsilon \tag{3.2}$$

$$X_{\max, out} = \frac{Y_s - b}{m} - \epsilon \tag{3.3}$$

The mass load of SO<sub>2</sub> transferred in kmol SO<sub>2</sub>/hr for each operation is given by:

$$g = G(Y_s - Y_t) \tag{3.4}$$

The minimum freshwater requirement of the process is to be determined by possible reuse of the water stream.

### 3.2 Petroleum Refining Complex

A petroleum refinery case study is presented to deal with the problem of multiple contaminants in process plants. Three water using operations commonly found in the petroleum industry are considered. These include a distillation unit using live steam injection, a hydrodesulphurization (HDS) reactor and a desalter. The last two processes use water to wash out contaminants. The limiting process data for three contaminants are given in Table 3.2 (Wang and Smith, 1994). Water can be regenerated using a foulwater stripper performing to a removal ratio of 0.0, 0.999 and 0.0 on hydrocarbon, H<sub>2</sub>S and salt, respectively. It is assumed that there is no change in flowrate through regeneration. Also, recycling in the system is not desired to avoid buildup of inorganics. The cost correlations used are taken from Takama et al. (1980) and shown in Table 3.3.

Table 3.2: Limiting process data for refinery case study

Process	water flowrate (te/hr)	contaminants	C <sub>in</sub> (ppm)	C <sub>out</sub> (ppm)
1. Distillation (Steam stripping)	45	hydrocarbon	0	15
		H <sub>2</sub> S	0	400
		salt	0	35
2. Hydrodesulphurization (HDS)	34	hydrocarbon	20	120
		H <sub>2</sub> S	300	12500
		Salt	45	180
3. Desalter	56	hydrocarbon	120	220
		H <sub>2</sub> S	20	45
		Salt	200	9500

Table 3.3 Economic data for the refinery case study

	Investment cost (\$)	Operating cost (\$/hr)
End of pipe treatment	$34200 f^{0.7}$	$1.0067 f$
Regenerative foulwater stripper	$16800 f^{0.7}$	$1.0 f$

Freshwater cost = 0.3 \$/te

Annual operation = 8600 hr/yr

Annualisation factor for capital cost = 0.1

The system is to be optimized for minimum freshwater requirements so as to reduce the total annual operating cost.

### SOLUTION TECHNIQUES

There are four general approaches to wastewater minimization (Wang and Smith, 1994):

1. *Process changes*: These are modifications in the process which reduce the inherent demand of water. An example is the replacement of wet cooling towers by dry air coolers.
2. *Water Reuse*: Wastewater can be directly used in other water using operations if the level of contaminants does not interfere with the water using operation. This reduces both freshwater and wastewater volumes but does not change the mass load of contaminant.
3. *Regeneration reuse*: Wastewater can be regenerated by partial or total treatment to remove the contaminants that prevent its reuse and then can be reused in other water using operations. Regeneration reduces both freshwater and wastewater volumes and decreases the mass load of contaminant.
4. *Regeneration Recycle*: Wastewater can be regenerated to remove contaminants and then the water recycled. In this case, regenerated water may be reused in water using operations in which the water stream has already been used.

This chapter lays out the basic principles for analyzing a water using operation and then compares the freshwater and wastewater flowrates for the systems with and without reuse. First, the system is defined as a mass transfer problem in which the contaminant is transferred from a contaminant rich process stream to a water stream. Next, the system is analyzed treating each water-using operation separately. Finally, the minimum freshwater requirement for the integrated system is determined by maximum water reuse. For this analysis, *the concentration composite curve, the concentration interval diagram and the freshwater pinch* are introduced. The methods of regeneration reuse and recycle are also discussed. The work of Wang and Smith (1994,1995) and Mann and Liu (1999) is extended and discussed to determine the minimum flowrate targets of freshwater and regenerated water.

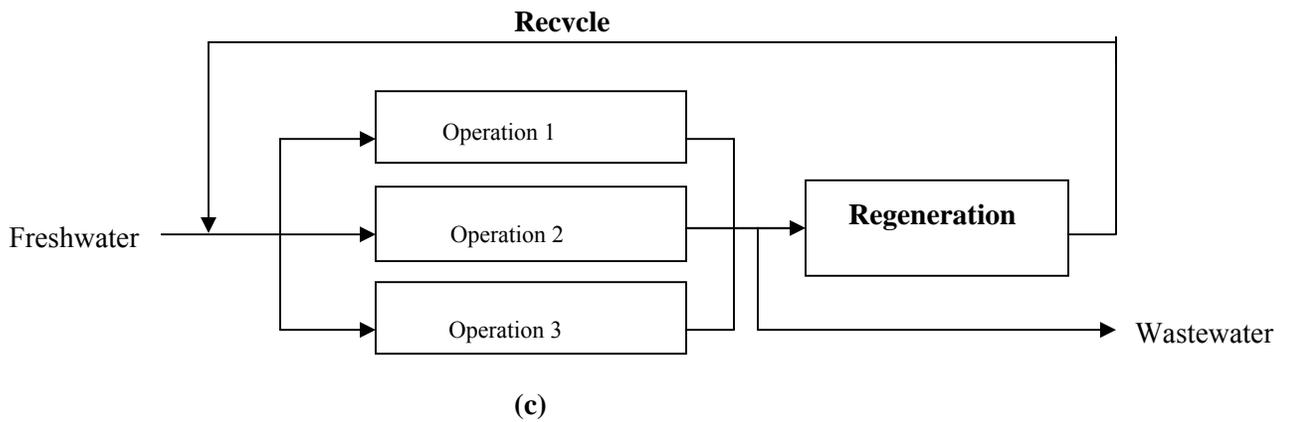
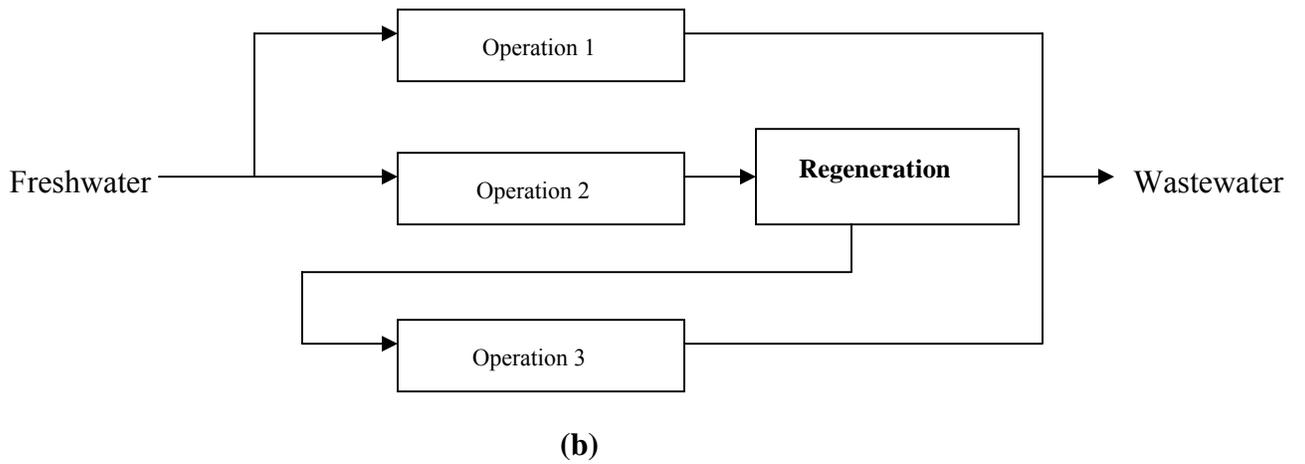
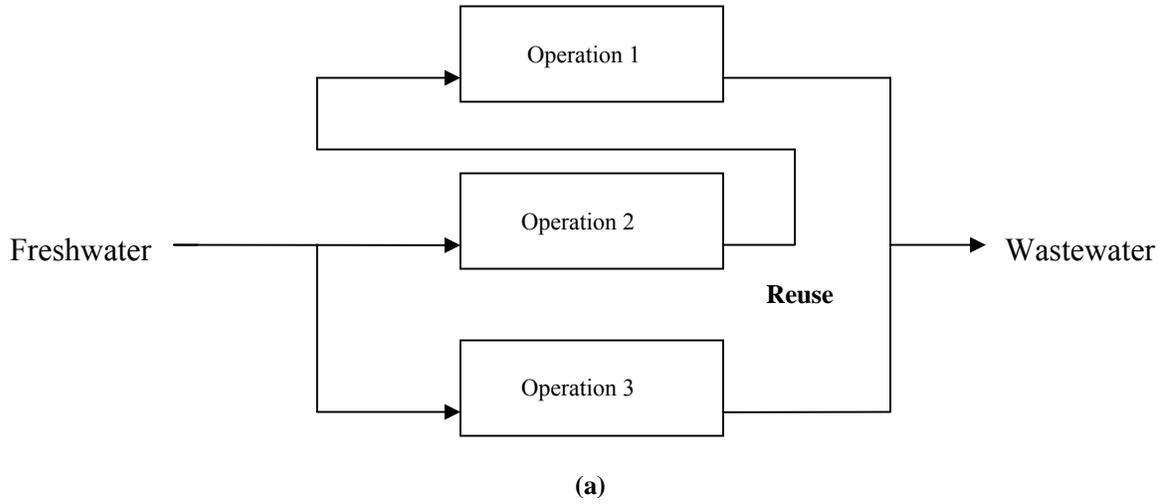


Figure 4.1 water minimization through (a) reuse, (b) regeneration reuse, and (c) regeneration recycle (Mann and Liu, 1999)

## 4.1 Water using operation as a mass transfer problem

An industrial water using operation can be represented as a mass transfer problem from a contaminant rich process stream to a water stream as shown in Fig 4.2 (Dhole et al,1996). The contaminants can be suspended solids, dissolved gases and other such impurities whose concentration levels prevent the reuse of the effluent water in the operation. In this case, the two streams approach from opposite directions in a countercurrent arrangement.

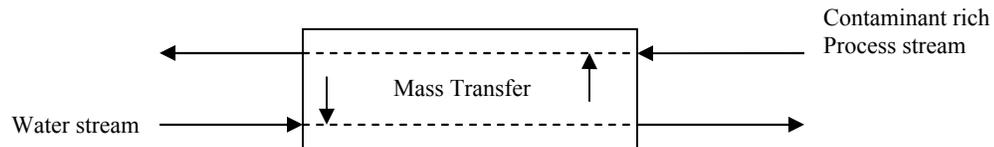


Figure 4.2 contaminant-rich process stream representation of a water using operation (Dhole et al, 1996)

## 4.2 Data Extraction

To analyze a water using operation, the constraints of the operation need to be identified and based on these constraints, the limiting water flowrate for that operation is determined. A constraint is anything that prevents a water stream from being reused. The basic constraints for operation  $i$  are (1) the contaminant level in the inlet streams,  $C_{i,in,lim}$  (2) the contaminant level in the outlet stream,  $C_{i,out,lim}$  and (3) the total mass load of contaminant to be transferred,  $\Delta m_{i,tot}$ . The water reuse is maximized when the constraints are just satisfied.

With these constraints the limiting water flowrate for operation  $i$  is calculated as,

$$f_{i, \text{lim}}(te / hr) = \frac{\Delta m_{i, \text{tot}}(kg / hr)}{[C_{i, \text{out, lim}} - C_{i, \text{in, lim}}](ppm)} \times 1000 \quad (4.1)$$

### 4.3 Minimum Freshwater Requirement without Reuse

The minimum freshwater flowrate required for each operation can be determined by using the limiting water profile. The limiting water profile is a plot of contaminant concentration versus mass load for a given set of constraints on water reuse.

.Fig 4.3 shows a general relationship between the limiting water profile and the water supply line for operation i. In the figure,  $C_{i,w,supply}$  and  $C_{i,w,out}$  are the contaminant concentration of the freshwater supply and the contaminant concentration of the water stream leaving operation i, respectively.

$$slope = \frac{\Delta C_i(ppm)}{\Delta m_{i,tot}(kg/hr)} \quad (4.2)$$

$$\begin{aligned} f_i(te/hr) &= \frac{\Delta m_{i,tot}(kg/hr)}{\Delta C_i(ppm)} \times 1000 \\ &= \frac{1}{slope} \times 1000 \end{aligned} \quad (4.3)$$

$$f_i(te/hr) = \frac{\Delta m_{i,tot}(kg/hr)}{[C_{i,w,out} - C_{i,w,in}](ppm)} \times 1000 \quad (4.4)$$

In the case of minimum freshwater flowrate,  $C_{i,w,in} = 0$  and  $C_{i,w,out} = C_{i,out,lim}$ . Eq. 4.1 becomes

$$f_{i,min}(te/hr) = \frac{\Delta m_{i,tot}(kg/hr)}{C_{i,out,lim}(ppm)} \times 1000 \quad (4.5)$$

The total freshwater flowrate without reuse is simply the sum of the minimum freshwater flowrates required by each operation:

$$f_{i,min}(te/hr) = \sum_i \frac{\Delta m_{i,tot}(kg/hr)}{C_{i,out,lim}(ppm)} \times 1000 \quad (4.6)$$

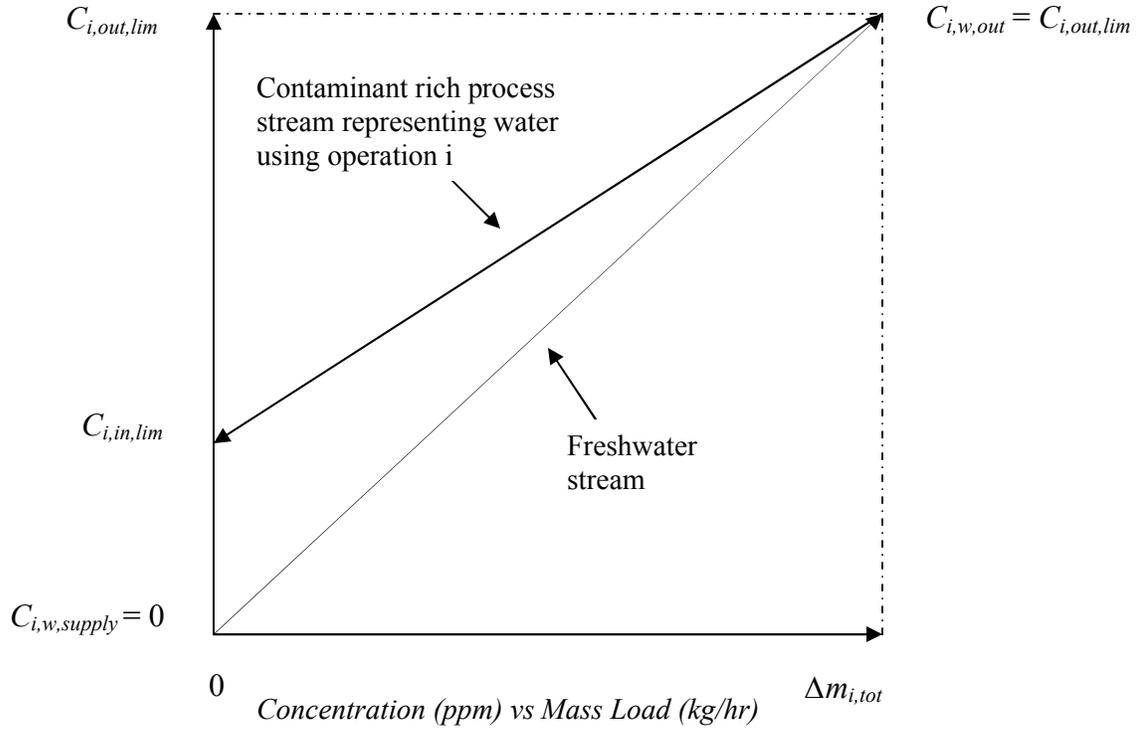


Figure 4.3 The relationship between the limiting water profile and the water supply line (Mann and Liu,1997)

#### 4.4 Minimum Freshwater Requirement with Reuse

##### 4.4.1 Graphical Approach: Composite Curve

In this method, the concentration composite curve of all water using operations is drawn, starting from an inlet contaminant concentration of zero for the freshwater supply to the average outlet concentration of the contaminant of all operations. This curve consists of a series of linear segments at increasing concentration intervals, representing the total mass load of the contaminant of all operations. The water supply line is then rotated counterclockwise about the origin (i.e. at zero inlet concentration and zero mass load) until it becomes tangent to the concentration composite curve to locate the freshwater pinch. The concentration at the pinch is given by  $C_{pinch}$ . The minimum freshwater flowrate becomes,

$$f_{\min}(te/hr) = \frac{\Delta m_{pinch}(kg/hr)}{C_{pinch}(ppm)} \times 1000 \quad (4.7)$$

#### 4.4.2 Tabular Method: Concentration Interval Diagram

The tabular method is based on the concept of concentration interval boundaries determined from the limiting inlet and outlet concentrations from the limiting process data. The flowrate at each concentration interval boundary is evaluated from the cumulative mass load and the interval boundary concentration.

$$f_k (te/hr) = \frac{\Delta m_k (kg/hr)}{C_k(ppm)} \times 1000 \quad (4.8)$$

The freshwater pinch occurs at the point with the greatest water supply flowrate. That flowrate is then the minimum required flow.

#### 4.5 Minimum Freshwater Requirement with Regeneration Reuse

The process of regeneration reduces the contaminant concentration in the water stream once it reaches the optimal regeneration concentration. All streams enter the regeneration process at a concentration of  $C_{regen}$ . This concentration is reduced to the minimum outlet concentration of the regeneration process,  $C_0$ . All streams exit at the same flowrate. The total flowrate is then constant before and after regeneration. For simple regeneration problems, the optimum regeneration concentration is the pinch concentration (Wang and Smith, 1994).

The mass load of contaminant transferred to the freshwater stream prior to regeneration is,

$$\Delta m_{regen} = f_{\min} C_{pinch} \quad (4.9)$$

The mass load of contaminant transferred to the regenerated water stream between the regeneration outlet concentration  $C_0$  and the freshwater pinch,  $C_{pinch}$ , is

$$\Delta m_{pinch} - \Delta m_{regen} = f_{\min}(C_{pinch} - C_0) \quad (4.10)$$

The total mass load of contaminant transferred prior to the freshwater pinch is the sum,

$$\Delta m_{pinch} = f_{min} C_{pinch} + f_{min}(C_{pinch} - C_0) \quad (4.11)$$

Rearranging Eq. (4.11), the minimum freshwater flowrate for simple full regeneration problems in terms of the freshwater pinch,  $C_{pinch}$  and the regeneration outlet concentration,  $C_0$  is,

$$f_{min}(te/hr) = \frac{\Delta m_{pinch}(kg/hr)}{[2C_{pinch} - C_0](ppm)} \times 1000 \quad (4.12)$$

Lastly, the outlet concentration of the regenerated water stream or the outlet concentration of the water supply line is given by,

$$C_{out}(ppm) = C_{pinch}(ppm) + \frac{[\Delta m_{tot} - \Delta m_{pinch}](kg/hr)}{f_{min}(te/hr)} \times 1000 \quad (4.13)$$

#### 4.6 Minimum Freshwater Requirement with Regeneration Recycle

Regeneration recycle is used to supply a wide range of flowrates of regenerated water to the region above the regeneration outlet concentration. The recycle flowrate can be greater than the minimum freshwater flowrate that is determined by the concentration composite curve in the region below  $C_0$ . The regenerated water flowrate is exactly equal to that required to pinch at the freshwater pinch (Wang and Smith, 1994).

The mass load of contaminant transferred prior to regeneration is,

$$\Delta m_{regen}(kg/hr) = \frac{f_{min}(te/hr)C_{pinch}(ppm)}{1000} \quad (4.14)$$

The flowrate of the wastewater to be regenerated is,

$$\begin{aligned}
 f_{regen}(kg/hr) &= \frac{\Delta m_{pinch} - \Delta m_{regen}}{C_{pinch} - C_0} \\
 &= \frac{\Delta m_{pinch}(kg/hr) - [f_{min}(te/hr)C_{pinch}(ppm)/1000]}{[C_{pinch} - C_0](ppm)} \times 1000
 \end{aligned} \tag{4.15}$$

The recycled water flowrate is simply the sum of the flowrates of freshwater and regenerated water.

$$f_{recycle} = f_{min} + f_{regen} \tag{4.16}$$

The average outlet concentration of the water supply line is given by,

$$C_{out}(ppm) = C_{pinch}(ppm) + \frac{[\Delta m_{tot} - \Delta m_{pinch}](kg/hr)}{f_{min}(te/hr)} \times 1000 \tag{4.17}$$

The basic concepts of reuse, regeneration reuse and regeneration recycle are used to develop mathematical code to generate computer aided solutions to a given problem. The input parameters are the inlet limiting concentrations, outlet limiting concentrations, the limiting flowrates and the regeneration outlet concentration. The minimum freshwater requirement for the system is obtained as the output. The MATLAB codes for the different processes are included in Appendix B.

An example is presented in Appendix C to illustrate the comparative study of given problem using the different methods discussed.

#### 4.7 Multiple Contaminants Problem

Most of the real life water using systems face the problem of multiple contaminants limiting the possibility of reusing the effluent from one operation in another water using operation. The approach to single contaminant problems can be applied to multiple contaminants, taking one of the contaminants as a reference contaminant,

provided other contaminants do not interfere with the transfer of the reference contaminant. The approach to a multiple contaminant problem is to target and design for the key contaminant and simulate the performance for non-key contaminants (Wang and Smith, 1994). The approach to single contaminant is extended to develop an approach to multiple contaminant systems with multiple constraints.

The basic concepts of waste water minimization in multiple contaminant systems are provided in the appendix to the article by Wang and Smith (1994). The approach has been extended and developed into a mathematical code to determine the minimum freshwater requirement of a multiple contaminant system using computer programming.

The concentrations of contaminant  $j$  at the inlet,  $n$ th concentration interval boundary and outlet of water using operation  $i$  is denoted as  $C_{ij,in}$ ,  $C_{ij,n}$  and  $C_{ij,out}$ , respectively. For two contaminants A and B, the proportional mass transfer relationship holds good (Mann and Liu, 1999),

$$\frac{C_{iA,n} - C_{iA,in}}{C_{iA,out} - C_{iA,in}} = \frac{C_{iB,n} - C_{iB,in}}{C_{iB,out} - C_{iB,in}} \quad (4.18)$$

The approach to single contaminant is extended to multiple contaminant systems by ensuring that the reuse of water leaving an operation is feasible with respect to other contaminants. To accomplish this, the contaminant concentration levels of each operation is shifted when plotting the limiting water profile, with respect to a reference operation and a reference contaminant, to ensure that the all the contaminant levels are in the feasible limit to be used in the next interval. This technique is called *concentration shift* (Wang and Smith, 1994). Two types of concentration shift are possible:

1. *Inlet concentration shift*: This involves shifting the inlet concentration of a reference contaminant in the receiving operation to a feasible point within the operation from which water will be reused.
2. *Outlet concentration shift*: This involves shifting the outlet concentration of the receiving operation until either of the contaminants becomes limiting.

The data from the final limiting water profiles obtained by concentration shifts is passed as an input to the program for single contaminant problem and the minimum freshwater required by the system is obtained as the output. An example is considered to illustrate the methodology for analysis of multiple contaminant problems in Appendix C.

The mathematical programming approach developed in this chapter is used for the analysis of the industrial case studies.

#### 4.8 Algorithm to develop the code for solution of problems

##### 4.8.1 Algorithm to develop code for wastewater minimization by reuse for single contaminant problem

1. The limiting process data for the problem is passed as input.
2. The maximum concentration  $C_{\max}$  is determined.
3. The concentration intervals are determined.
4. The sum of limiting flowrates in each interval is calculated.
5. The mass load in each interval is calculated by the formula

$$ml_k = \frac{C_{k+1} - C_k}{1000} \times \sum_k f_{i, \text{lim}}$$

where,

$ml_k$  = mass load in  $k^{\text{th}}$  concentration interval, kg/hr

$C_{k+1}$  = outlet concentration of  $k^{\text{th}}$  concentration interval, ppm

$C_k$  = inlet concentration of  $k^{\text{th}}$  concentration interval, ppm

$f_{i, \text{lim}}$  = limiting flowrate of operation  $i$  in  $k^{\text{th}}$  concentration interval, kg/hr

6. The cumulative mass load in each interval is calculated.

$$cm_k = \sum_{i=1}^k ml$$

7. The flowrate of water is calculated at each concentration interval boundary as

$$f_k = \frac{cm_k}{C_k} \times 1000$$

8. The highest flowrate of water is the required minimum freshwater flowrate and the corresponding concentration interval boundary is the freshwater pinch concentration.

#### 4.8.2 Algorithm to develop code for wastewater minimization by regeneration reuse for single contaminant problem

1. The limiting process data as well as the regeneration outlet concentration,  $C_0$  is passed as an input.
2. Steps 2-7 for single contaminant reuse problem are repeated except that  $C_0$  is also included as a concentration interval boundary.
3. The location of the freshwater pinch corresponding to the highest flowrate is determined.
4. The flowrate of regenerated water is calculated as,

$$f_{regen} = f_{\min} = \frac{\Delta m_{pinch}}{2C_{pinch} - C_0} \times 1000$$

where,

$\Delta m_{pinch}$  = cumulative mass load corresponding to freshwater pinch,  
kg/hr

$C_{pinch}$  = freshwater pinch concentration, ppm

5. The outlet concentration of the regenerated water stream is calculated as,

$$C_{out} = C_{pinch} + \frac{\Delta m_{tot} - \Delta m_{pinch}}{f_{\min}} \times 1000$$

where,

$\Delta m_{tot}$  = total cumulative mass load, kg/hr

#### 4.8.3 Algorithm to develop code for wastewater minimization by regeneration recycle for single contaminant problem

1. The limiting process data as well as the regeneration outlet concentration,  $C_0$  is passed as an input
2. Steps 2-7 for single contaminant reuse problem are repeated except that  $C_0$  is also included as a concentration interval boundary.
3. The flowrate corresponding to  $C_0$  interval boundary is equal to  $f_{min}$ .
4. The location of the freshwater pinch corresponding to the highest flowrate is determined.
5. The flowrate of regenerated water is calculated as

$$f_{regen} = \frac{\Delta m_{pinch} - [f_{min} \times C_{pinch} / 1000]}{[C_{pinch} - C_0]} \times 1000$$

6. The flowrate of recycled water is calculated as,

$$f_{recycle} = f_{regen} + f_{min}$$

## RESULTS AND DISCUSSIONS

### 5.1 Case study: SO<sub>2</sub> extraction problem

#### 5.1.1 Minimum freshwater flowrate required for the system

Table 5.1 Limiting process data for problem SO<sub>2</sub> extraction problem

Operation	$X_{in,max} * 10^3$ (kmol SO <sub>2</sub> /kmol H <sub>2</sub> O)	$X_{out,max} * 10^3$ (kmol SO <sub>2</sub> /kmol H <sub>2</sub> O)	g (kmol SO <sub>2</sub> /hr)	$f_{lim} * 10^{-3}$ (kmol H <sub>2</sub> O/hr)
1	0.2932	0.5030	0.3	1.305
2	0.3115	0.5030	0.3	1.566
3	0.3115	0.8862	0.6	1.044
4	0.6946	0.8862	0.15	0.783

The limiting process data is passed as an input to program 1 in Appendix B and the minimum freshwater requirement for the system is obtained as output.

The minimum freshwater requirement for the system without reuse is 2040 kmol/hr and with reuse it is found to be 1589 kmol/hr.

The output data obtained is used to plot the concentration composite curve for the process as shown in Fig. 5.1. The tangent to this line gives the water supply line. This plot is used for designing the mass exchange network for the SO<sub>2</sub> extraction problem.

#### 5.1.2 Design of network

The preliminary design of the network is shown in Fig 5.2. The detailed calculation for the preliminary network design is given in Appendix A. The loops in the preliminary design are marked by A, B and C. The network is simplified by loop breaking to reduce the number of mass transfer units and to optimize the system. The detailed calculation of loop breaking to simplify the network is given in Appendix A. Fig 5.3 represents the simplified network after loop breaking.

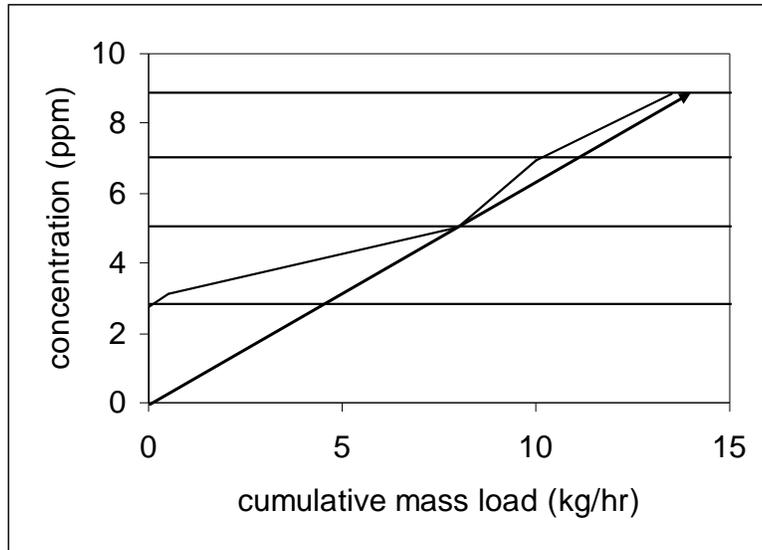


Figure 5.1 Concentration composite curve for SO<sub>2</sub> extraction problem

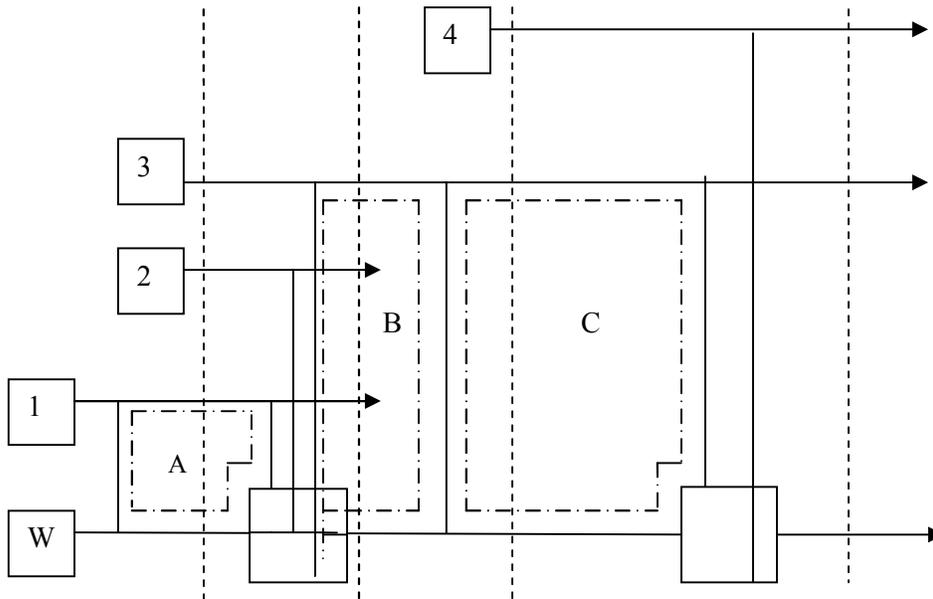


Figure 5.2 Preliminary design of the network for SO<sub>2</sub> extraction problem

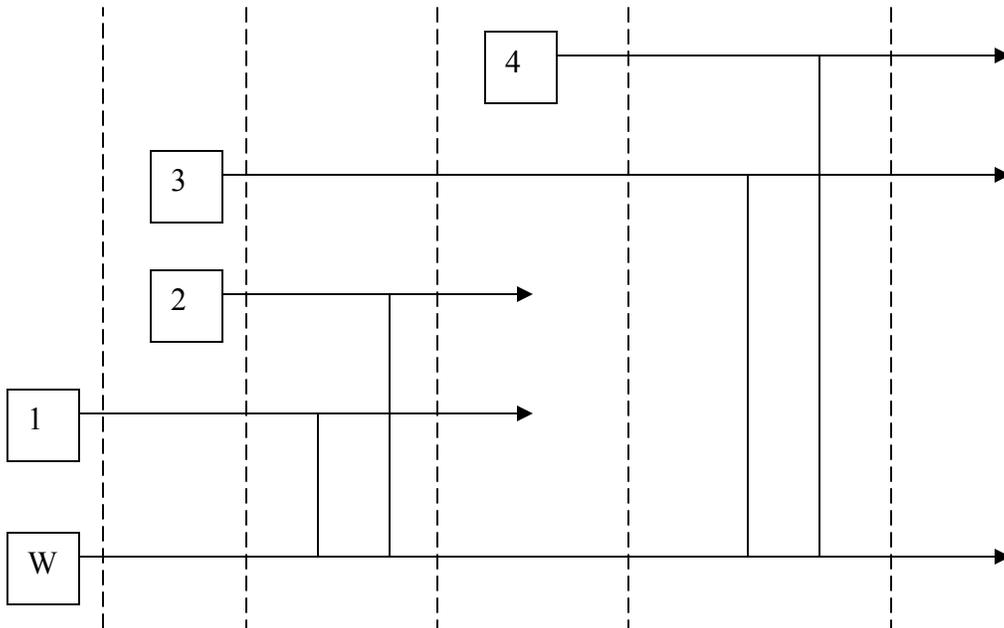


Figure 5.3 Simplified network design after loop breaking

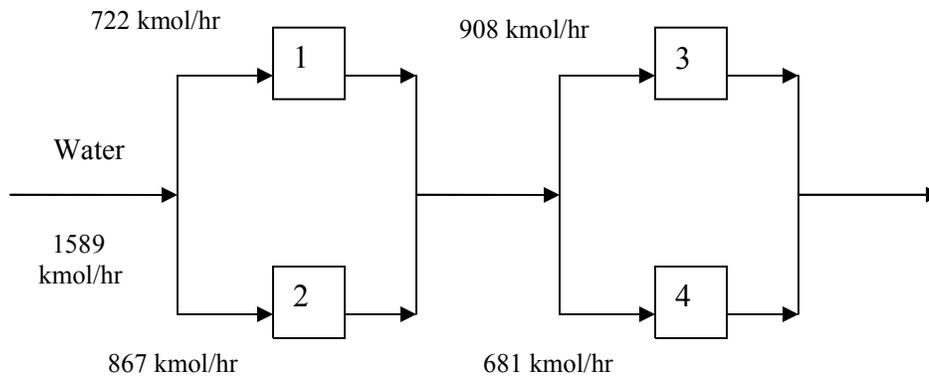


Figure 5.4 Block Diagram of the final network

### 5.1.3 Discussion

The process of reuse leads to a reduction of about 22% in the freshwater requirement over the system without reuse. The process of loop breaking in the design of the mass exchange network reduces the number of units required by 3 units and thus simplifies the network as well as reduces the capital cost.

## 5.2 Case study: Petroleum Refining Complex

The petroleum refining complex is analyzed by taking H<sub>2</sub>S as the reference contaminant and operation 1 as the reference operation. The limiting water profiles for the problem with respect to H<sub>2</sub>S are provided in Appendix A. The limiting water profiles are plotted using the algorithm by Wang and Smith (1994). The data from the limiting water profiles after concentration shift is used to determine the minimum freshwater requirement for the system.

### 5.2.1 Result

Table 5.2 contrasts the three alternatives to determine the minimum freshwater requirement for the case study i.e. without reuse, reuse without regeneration and reuse with regeneration.

Table 5.2 Summary of the three alternatives for the case study

	Wastewater Flowrate (te/hr)	Freshwater cost (MMS\$/hr)	Treatment capital cost (MMS\$/yr)	Treatment operating cost (MMS\$/yr)	Total annual cost (MMS\$/yr)
1. Without reuse	133	0.343	1.049	1.159	1.599
2. Reuse without regeneration	107	0.276	0.901	0.926	1.292
3. Reuse with regeneration	54	0.139	0.839	0.931	1.154

For the process of regeneration, a regeneration outlet concentration  $C_0 = 10$  ppm is used for the analysis. The outlet concentration of the water supply is found to be  $C_{out} = 8014$  ppm.

### 5.2.2 Design of network

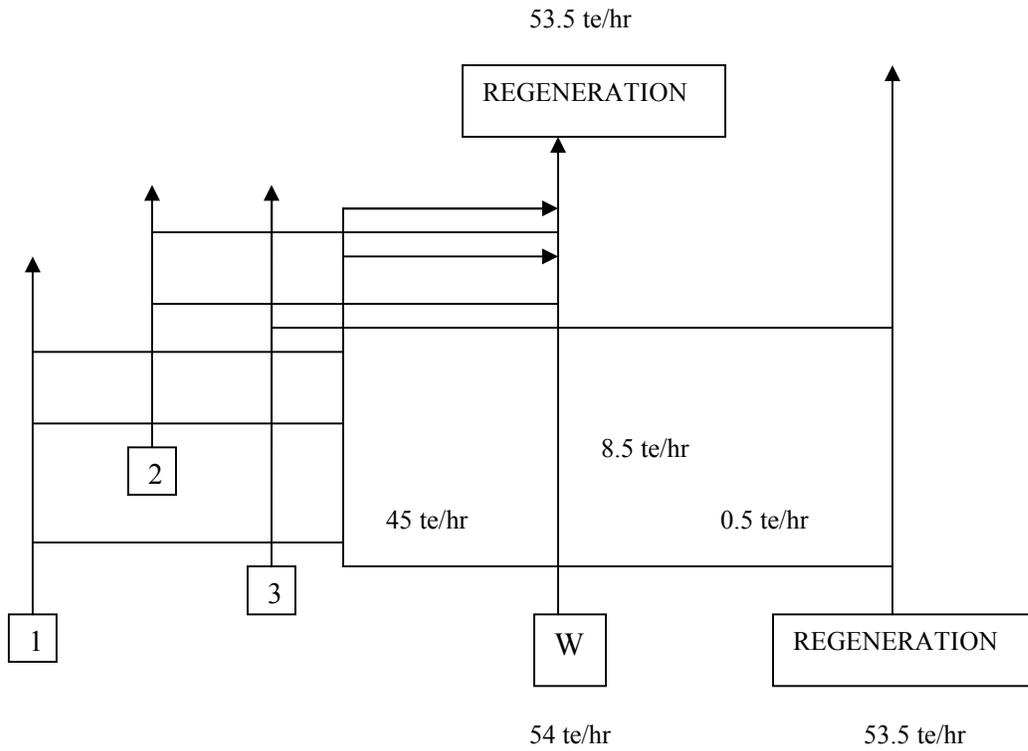


Figure 5.5 Preliminary network design for petroleum refinery after regeneration reuse

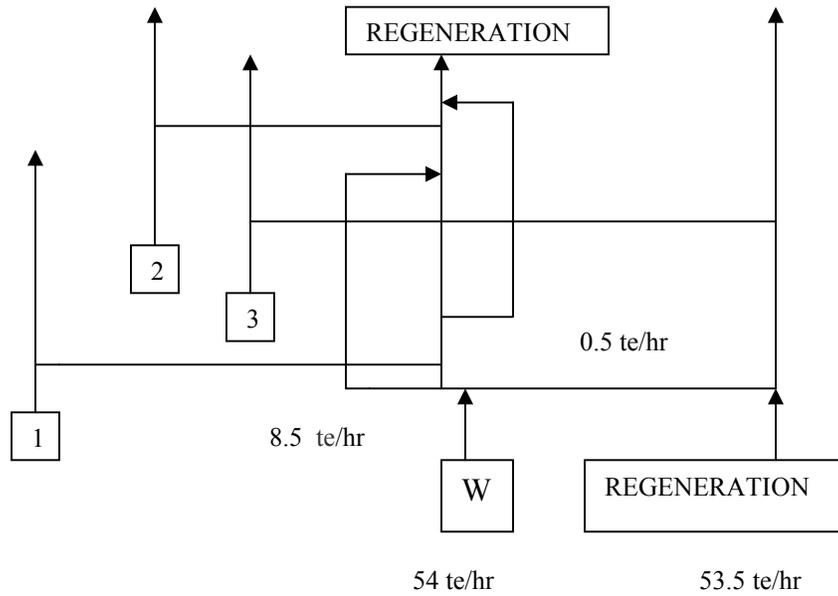


Figure 5.6 Evolved network design for petroleum refinery

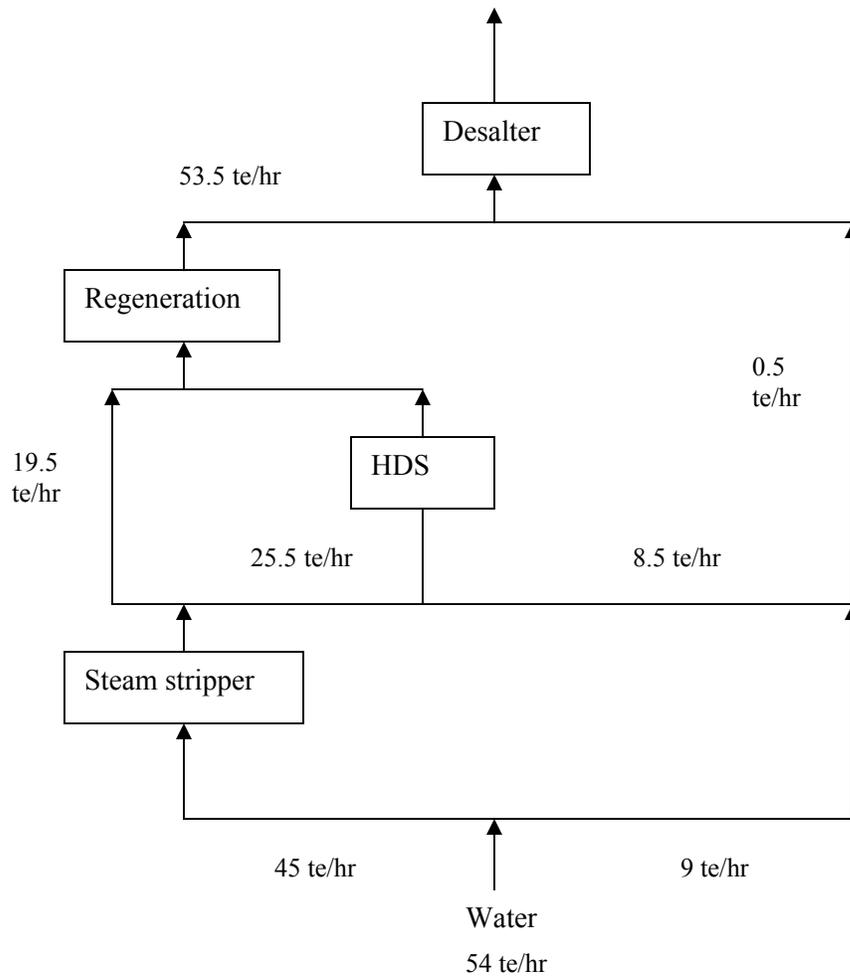


Figure 5.7 Flowsheet for the evolved design for petroleum refinery

### 5.2.3 Discussion

The freshwater flowrate required by the refinery complex and the total annual cost are reduced by the process of reuse and regeneration reuse. The process of reuse without regeneration brings a reduction of about 20 % in the annual cost and the process of regeneration with reuse brings a reduction of about 28 % in the cost relative to system without reuse. The results obtained by mathematical programming are consistent with the analytical solution provided by Wang and Smith (1994) with an error of only about 1%.

## Chapter 6

### CONCLUSION

The methods of reuse, regeneration reuse and regeneration recycle have been discussed to reduce the freshwater requirement as well wastewater generation in a wide range of processes. The limiting process data is used to plot the limiting water profiles. The targets for freshwater, regeneration and wastewater flowrates are set using the limiting water profiles. The design of the network is subjected to constraints such as minimum mass transfer driving forces, equipment fouling, corrosion limitations etc. The approach to single contaminant problem can be extended to multiple contaminants problem by incorporating inlet and outlet concentration shifts. Wastewater streams can be fully or partially regenerated by physical, chemical or biological methods to remove the contaminants that limit its reuse in other processes

The following conclusions can be drawn from the application of the methods discussed in this thesis to the industrial case studies:

1. There is a significant decrease in the minimum freshwater requirement of a system with the reuse and regeneration of wastewater as compared to systems without reuse. The reduction in freshwater requirement with reuse for the SO<sub>2</sub> extraction system is 22 % and that for the petroleum refinery is 20 %.
2. The process of regeneration reuse gives a greater reduction in minimum freshwater requirement as compared to only reuse but the processes of regeneration reuse and recycle are subject to constraints such as buildup of undesired components. The reduction in freshwater requirement with regeneration reuse for the petroleum refinery complex is about 60 %.
3. The flowrates of freshwater and regenerated water are identical, and these flowrates are minimum when the regeneration concentration is equal to the

freshwater pinch concentration i.e. the water is allowed to reach the pinch concentration before regeneration.

4. The concentration interval design method can be successfully utilized to design the preliminary water-using network that meets the minimum freshwater flowrate subject to the limiting constraints. The application of loop breaking simplifies the water using network and reduces the number of water using units.
5. The reduction of freshwater requirement by reuse and regeneration leads to a decrease in the total annual operating cost of the system.

Thus the process of wastewater minimization through pinch analysis is a powerful tool in process integration and plays a significant role design of the conventional water reuse project, by identifying a minimum freshwater flowrate and key water reuse opportunities.

## REFERENCES

1. Bagajewicz, M. J., Pham, R. and Manousiouthakis, V., “*On the state space approach to mass/heat exchanger network design*”, Chem Eng Sci, 53(14), 1998
2. Dhole, V. R., Ramchandani, N., Tainsh, R. A. and Wasilewski, M., “*Make your process water pay for itself*”, Chemical Engineering, 103, 1996
3. El-Halwagi, M. M. and Manousiouthakis, V., “*Synthesis of mass exchange networks*”, AIChE Journal, 35, 1989
4. Foo, C. Y., Manan, Z. A., Yunus, R. M. Aziz, R. A. and Tan, Y. L., “*Maximising Water Recovery through Water Pinch Technology – The Use of Water Cascade Table*”, Universiti Teknologi Malaysia, 2006
5. Hallale, N., and Fraser, D.M., “*Supertargeting for mass exchange networks Part I: Targeting and Design Techniques*”, Trans IChemE, 78 A, 2000
6. Hallale, N., “*A new graphical targeting method for water minimisation*”. Adv. Env. Res., 6 (3), 2002
7. Linnhoff, B., and Flower, J.R., “*Synthesis of Heat Exchanger Networks. Part I. Systematic generation of energy optimal networks*”, AIChE J., 24, 1978
8. Linnhoff, B., Townsend, D. W., Boland, D., Hewitt, G. F., Thomas, B. E. A., Guy, A. R. and Marshall, R. H., “*A user guide on process integration for the efficient use of energy*”. IChemE, Rugby, UK, 1982
9. Linnhoff, B., “*Pinch analysis: A state-of-the-art overview*”, Trans IChemE, Part A, 71, 1993
10. Mann, James. G and Liu, Y.A, “*Industrial Water Reuse and Wastewater Minimization*”, McGraw Hill, 1999
11. Papalexandri, K. P., Pistikopoulos, E. N., and Floudas, C. A., “*Mass exchange networks for waste minimisation: A simultaneous approach*”, Trans IChemE, Part A, 72, 1994
12. Querzoli, Adrian L., Hoadley, Andrew F. A and Dyson, Tony E. S., “*Identification of Heat Integration Retrofit Opportunities for Crude Distillation and Residue Cracking Units*”, Korean J. Chem. Eng, 20(4), 2003

13. Savelski, M. J. and Bagejewicz, M. J., “*On the optimality conditions of water utilization systems in process plants with single contaminants*”. Chem Eng. Sci. ,55, 2000
14. Takama, N., Kuriyama, T., Shiroko, K. and Umeda, T. “*Optimal water allocation in a petroleum refinery*”, Computers Chem. Eng., 4,1980.
15. Tan, Y. L., Manan, Z. A. and Foo, C. Y., “*Water minimisation by pinch technology – water cascade table for minimum water and wastewater targeting*”. 9<sup>th</sup> Asian Pacific Confederation of Chemical Engineering (APCCChE 2002) Congress
16. Wang, Y. P. and Smith, R., “*Wastewater minimisation*”. Chem. Eng. Sci., 49, 1994

## APPENDIX A

### DETAILED SOLUTION TO THE CASE STUDY PROBLEMS

#### A.1 Case study: SO<sub>2</sub> extraction problem

The limiting process data for the problem is obtained by using equations 3.2, 3.3 and 3.4 and is presented in Table 5.1

The data is passed as an input to the code for single contaminant problem in Appendix B and the output is obtained.

Input

$$c_{in} = [2.732 \ 3.115 \ 3.115 \ 6.946]$$

$$c_{out} = [5.030 \ 5.030 \ 8.862 \ 8.862]$$

$$f_{lim} = [1305 \ 1566 \ 1044 \ 783]$$

Output

$$f_{min} = 1.5899e+003$$

##### A.1.1 Design of mass exchange network

The freshwater supply line in the concentration composite curve is used to determine the inlet and outlet concentrations in each interval. This data can be used to determine the mass load of contaminant transferred in each operation in every interval. This is the mass load on the mass exchange units.

The minimum freshwater flowrate with reuse is found to be 1589 kmol/hr.

The mass load of contaminant transferred in each operation in each interval is calculated as,

$$m_{i,j} = \frac{f_{i,j}(C_{i,out} - C_{i,in})}{1000}$$

where,

$m_{i,j}$  = mass load of contaminant transferred in operation  $i$  in interval  $j$ , kmol of SO<sub>2</sub>/hr

$f_{i,j}$  = flow rate of water to operation  $i$  in interval  $j$ , kmol/hr

$C_{j,in}$  = concentration of contaminant in the water stream at the inlet of interval  $j$ ,

kmol of SO<sub>2</sub> / kmol of H<sub>2</sub>O

$C_{j,out}$  = concentration of contaminant in the water stream at the outlet of interval j,

kmol of SO<sub>2</sub> / kmol of H<sub>2</sub>O

### Interval 1

$$f_{1,1} = 1589$$

$$C_{1,in} = 0; C_{1,out} = 0.32$$

$$m_{1,1} = 1589 \times (0.32 - 0) = 0.508$$

### Interval 2

Ratio of limiting flowrates = 1.305:1.566: 1.044

The water supply flowrate is in the ratio of the limiting flowrates

Thus,

$$f_{1,2} = 529.7; f_{2,2} = 635.6; f_{3,2} = 423.7$$

$$C_{2,in} = 0.32; C_{2,out} = 5.03$$

$$m_{1,2} = 2.49; m_{2,2} = 2.99; m_{3,2} = 1.99$$

### Interval 3

$$f_{3,3} = 1589$$

$$C_{3,in} = 5.03; C_{3,out} = 6.30$$

$$m_{3,3} = 2.02$$

### Interval 4

Ratio of limiting flowrates = 1.044:0.7833

$$f_{3,4} = 907.9; f_{4,4} = 681.1$$

$$C_{4,in} = 6.30; C_{4,out} = 8.50$$

$$m_{3,4} = 1.99; m_{4,4} = 1.49$$

## B.1.2 Calculations for loop breaking

The loops in the system are identified as A, B and C. To combine the water using units, we shift the mass load of contaminant from one unit to another unit in the same

loop and then recalculate the outlet concentration of the water stream from the combined unit. These shifts can be imposed if and only if the results do not violate the limiting process data.

### **Loop A**

In loop A the water using unit in interval 1 has a mass load of 0.508 kmol of SO<sub>2</sub>/hr and the water using unit in interval 2 has a mass load of 2.49 kmol of SO<sub>2</sub>/hr. The load of the former is transferred to the latter and the outlet concentration of water from the interval 2 is recalculated.

$$C_{in} = 0$$

$$m = 0.508 + 2.49 + 2.99 = 5.99 \text{ kmol of SO}_2/\text{hr}$$

$$C_{out} = 0 + (5.99/1589) \times 1000 = 3.77 \text{ kmol of SO}_2/\text{ kmol of H}_2\text{O}$$

This outlet concentration is less than the limiting outlet concentration for interval 2 i.e. 5.03 kmol of SO<sub>2</sub>/ kmol of H<sub>2</sub>O. Hence the shift is feasible.

### **Loop B and C**

In loop B the water using unit in interval 2 has a mass load of 1.99 kmol of SO<sub>2</sub>/hr and the water using unit in interval 3 has a mass load of 2.02 kmol of SO<sub>2</sub>/hr. In loop C the water using unit in interval 3 has a mass load of 2.02 kmol of SO<sub>2</sub>/hr and the water using unit in interval 4 has a mass load of 1.99 kmol of SO<sub>2</sub>/hr. The mass load of operation 3 in the intervals 2 and 3 are transferred to interval 4. The outlet concentration of water leaving interval 4 is then recalculated.

$$C_{in} = 3.77$$

$$m = 1.99 + 2.02 + 1.99 + 1.49 = 7.49 \text{ kmol of SO}_2/\text{hr}$$

$$C_{out} = 3.77 + (7.49/1589) \times 1000 = 8.48 < 8.50$$

Hence the shift is feasible.

## **A.2 Case study: Petroleum refining complex**

The limiting water profile for the petroleum refinery case study with respect to H<sub>2</sub>S is represented in Fig A.1. H<sub>2</sub>S is chosen as the reference contaminant and operation 1

as the reference operation. A mass load axis is not included due to the large mass load of contaminant H<sub>2</sub>S in operation 2.

The inlets to operations 2 and 3 for feasibility of water are examined for feasibility of reuse. From Fig. A.1, it is clear that both operations do not require an inlet concentration shift.

The outlets of all three operations are then examined for feasibility. Operations 2 and 3 will not have reuse due to the high outlet concentrations of H<sub>2</sub>S in operation 2 and salt in operation 3. In addition, the outlet concentration of H<sub>2</sub>S in operation 1 does not allow the reuse of water leaving operation 1 into operation 3.

The only possibility is to reuse water leaving operation 1 at some point in operation 2. From Fig. A.1, it is seen that H<sub>2</sub>S is just limiting at the fifth concentration-interval boundary in operation 2, whereas hydrocarbons and salt concentrations are feasible. The outlet of operation 3 is shifted to the concentration interval boundary created at the outlet of operation 1. Fig. A.2 gives the resulting limiting water profile following this outlet concentration shift.

The inlet and outlet contaminant concentration of the water stream at each concentration interval is obtained from Fig. A.2. This data is then passed as the input to code for single contaminant problem given in Appendix B and the output is obtained.

Input

cin = [0 300 20]

cout = [400 12500 400]

flim = [45 34 56]

Output

fmin = 106.7

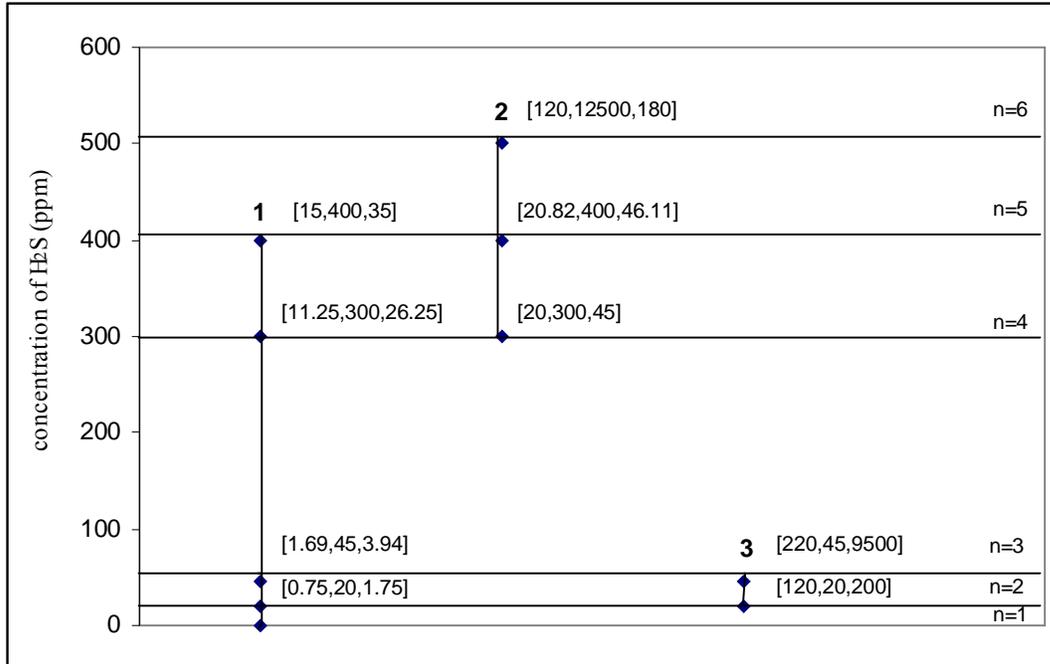


Figure A.1 Limiting water profiles for H<sub>2</sub>S in the petroleum refinery case study prior to concentration shifts

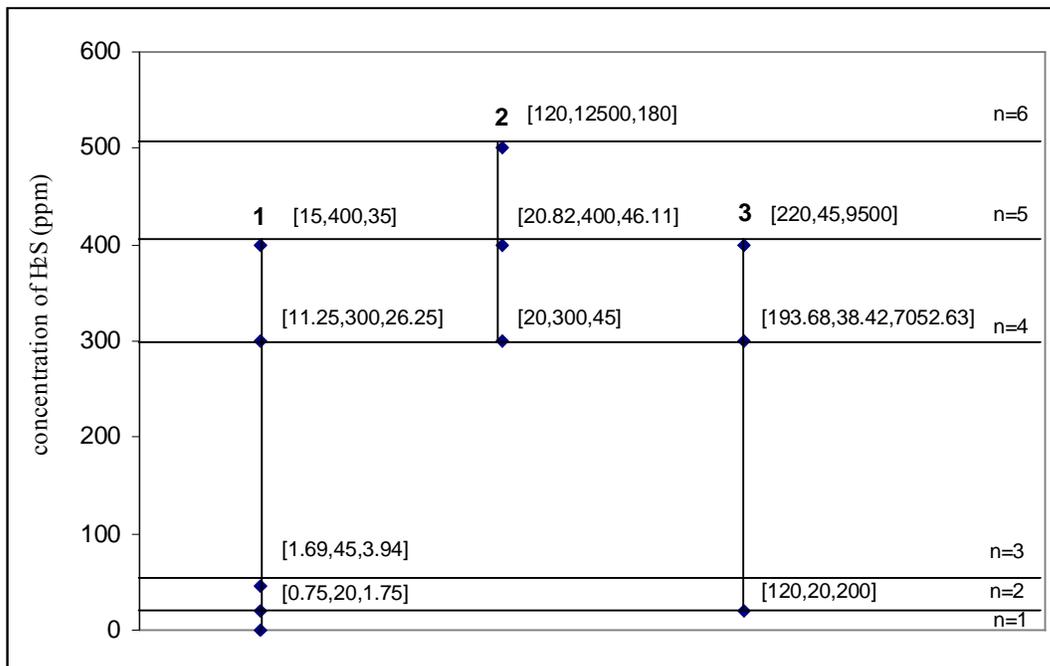


Figure A.2 Limiting water profiles for H<sub>2</sub>S in the petroleum refinery case following an outlet concentration shift on operation 3

For the determination of minimum freshwater flowrate the input is passed to the code for regeneration reuse in Appendix B and the output is obtained.

Input

$c_0 = 10$

$c_{in} = [0 \ 300 \ 20]$

$c_{out} = [400 \ 12500 \ 400]$

$f_{lim} = [45 \ 34 \ 56]$

Output

$f_{regen} = 54.0253$

$f_{min} = 54.0253$

$c_{out} = 8.0149e+003$

## APPENDIX B

### **MATLAB codes for the solution of problems using the methods of reuse, regeneration reuse and regeneration recycle.**

#### B.1.1 Determination of minimum freshwater flowrate for single contaminant problem with water reuse

```
% Passing as input the no. of operations in the system

n= input('enter no. of operations ')

% Passing as input the limiting process data
load m.txt
load cin.txt
load cout.txt
load flim.txt

% Determination of maximum contaminant concentration

max=0;
for x = 1:n
    if (cout(l) > max)
        max=cout(x)
    end
end

% Determination of concentration intervals

k=2;
for x = 1:0.001:max
    for y = 1:n
        if (cin(y) == x)
            c(k)=cin(y);
            k=k+1;
            break;
        end
        if (cout(y) == x)
            c(k)=cout(y);
            k=k+1;
            break;
        end
    end
end
end
k=k-1;
```

% Determination of sum of limiting flowrates in each interval

```
for x=2:k
    fl(x-1)=0;
    for y=1:n
        if (c(x-1)>=cin(y) & c(x)<=cout(y))
            fl(x-1)= fl(x-1)+flim(y);
        end
    end
end
```

% Determination of mass load in each interval

```
for x=1:k-1
    ml(x)= (c(x+1)-c(x))/(10*10*10)*fl(x);
end
```

% Determination of cumulative mass loads

```
cm(1)=0;
cm(2)=ml(1);
for x= 2:k
    cm(x)=0;
    for y= 1:x-1
        cm(x)=cm(x)+ml(y);
    end
end
```

% Determination flowrate of water in each interval

```
f(1)=0
for x= 2:k
    f(x)= (cm(x)/c(x))*(10*10*10)
end
```

% Determination of the minimum freshwater flowrate required

```
fmin=0;
for x= 1:k
    if(f(x)>fmin)
        fmin = f(x);
    end
end
fmin
```

```
% Creating output file
```

```
save('output','cm','fmin','ml','c');
```

### **B.1.2 Determination of minimum freshwater flowrate for single contaminant problem with regeneration reuse**

```
% Passing as input the no. of operations in the system
```

```
n= input('enter no. of operations ')
```

```
% Passing as input the limiting process data
```

```
load m.txt
```

```
load cin.txt
```

```
load cout.txt
```

```
load flim.txt
```

```
% Passing as input the regeneration outlet concentration
```

```
c0 = input('enter regeneration outlet concentration ')
```

```
% Determination of maximum contaminant concentration
```

```
max=0;
```

```
for l = 1:n
```

```
    if (cout(l) > max)
```

```
        max=cout(l)
```

```
    end
```

```
end
```

```
% Determination of concentration intervals
```

```
k=2;
```

```
for x = 1:0.001:max
```

```
    for y = 1:n
```

```
        if (cin(y) == x)
```

```
            c(k)=cin(y);
```

```
            k=k+1;
```

```
            break;
```

```
        end
```

```
        if(c0 == x)
```

```
            c(k)= c0
```

```
            z=k
```

```
            k=k+1
```

```
            break;
```

```

        end
        if (cout(y) == x)
            c(k)=cout(y);
            k=k+1;
            break;
        end
    end
end
k=k-1;

```

% Determination of sum of limiting flowrates in each interval

```

for x=2:k
    fl(x-1)=0;
    for y=1:n
        if (c(x-1)>=cin(y) & c(x)<=cout(y))
            fl(x-1)= fl(x-1)+flim(y);
        end
    end
end
end

```

% Determination of mass load in each interval

```

for x=1:k-1
    ml(x)= (c(x+1)-c(x))/(10*10*10)*fl(x);
end

```

% Determination of cumulative mass loads

```

cm(1)=0;
cm(2)=ml(1);
for x= 2:k
    cm(x)=0;
    for y= 1:x-1
        cm(x)=cm(x)+ml(y);
    end
end
end

```

% Determination flowrate of water in each interval

```

f(1)=0
for x= 2:k
    f(x)= (cm(x)/c(x))*(10*10*10)
end
end

```

```

% Determination of the minimum freshwater flowrate required without regeneration

fmin=0;
for x= 1:k
    if(f(x)>fmin)
        fmin = f(x);
        q=x;
    end
end

% Determination of the minimum freshwater flowrate required with regeneration reuse

fregen = cm(q)/((2*c(q))-c0)*1000;
fmin=fregen;

% Determination of the minimum freshwater flowrate required with partial
regeneration

fpar = 0;
funregen = 0;
if(fregen < f(z))
    fpar=f(z);
    fmin=fpar;
    fregen=(cm(q)- (fpar*c(q)/1000))/(c(q)-c0)*1000;
    funregen= fpar-fregen;
end

% Determination of outlet concentration of supply water
cout= c(q)+ (cm(k)-cm(q))/fmin*1000

% Creating output file
save('output1','cm','fmin','ml','fpar','fregen','funregen','c');

```

### **B.1.2 Determination of minimum freshwater flowrate for single contaminant problem with regeneration recycle**

```

% Passing as input the no. of operations in the system

n= input('enter no. of operations ')

% Passing as input the limiting process data

load m.txt
load cin.txt
load cout.txt
load flim.txt

```

```

% Passing as input the regeneration outlet concentration

c0 = input('enter regeneration outlet concentration ')

% Determination of maximum contaminant concentration

max=0;
for l = 1:n
    if (cout(l) > max)
        max=cout(l)
    end
end

% Determination of concentration intervals

k=2;
for x = 1:0.001:max
    for y = 1:n
        if (cin(y) == x)
            c(k)=cin(y);
            k=k+1;
            break;
        end
        if(c0 == x)
            c(k)= c0
            z=k
            k=k+1
            break;
        end
        if (cout(y) == x)
            c(k)=cout(y);
            k=k+1;
            break;
        end
    end
end
k=k-1;

% Determination of sum of limiting flowrates in each interval

for x=2:k
    fl(x-1)=0;
    for y=1:n
        if (c(x-1)>=cin(y) & c(x)<=cout(y))

```

```

        fl(x-1)= fl(x-1)+flim(y);
    end
end
end

% Determination of mass load in each interval

for x=1:k-1
    ml(x)= (c(x+1)-c(x))/(10*10*10)*fl(x);
end

% Determination of cumulative mass loads

cm(1)=0;
cm(2)=ml(1);
for x= 2:k
    cm(x)=0;
    for y= 1:x-1
        cm(x)=cm(x)+ml(y);
    end
end

% Determination flowrate of water in each interval

f(1)=0
for x= 2:k
f(x)= (cm(x)/c(x))*(10*10*10)
end

% Determination of the minimum freshwater flowrate required without regeneration

fmin=0;
for x= 1:k
    if(f(x)>fmin)
        fmin = f(x);
        q=x;
    end
end
fmin=f(z)

% Determination of the minimum freshwater flowrate required with regeneration
recycle

mregen= (f(z)*c(q))/1000;
fregen = (cm(q)-(f(z)*c(q)/1000))/(c(q)-c0)*1000;
frecycle= f(z)+fregen;

```

```
% Determination of outlet concentration of supply water  
cout= c(q)+(cm(k)-cm(q))/f(z)*1000
```

```
% Creating output file  
save('output','cm','fmin','ml','fregen','frecycle','c');
```

### **Variable Declaration**

n – counter for number of operations in the problem

m – mass load of contaminant in each interval

cin – limiting inlet concentration of water entering an interval

cout – limiting outlet concentration of water leaving an interval

flim – limiting water flowrate of an operation

c0 – regeneration outlet concentration

c – concentration of water at concentration interval boundary

fl – sum of limiting flowrates in an interval

ml – mass load of contaminant transferred in an interval

cm – cumulative mass load in an interval

f – flowrate of water in each interval

fmin – minimum freshwater flowrate required by the system

fregen – flowrate of regenerated water

frecycle – flowrate of recycled water

fpar – flowrate of partially regenerated water

funregen – flowrate of unregenerated water

x, k, y - counters

## APPENDIX C

### SOLUTION OF EXAMPLE PROBLEMS

#### C.1 Example 1: Comparison of the Minimum Freshwater Requirement for a given problem with the different methods

An example problem is considered from Wang and Smith (1994) to compare the minimum freshwater requirements for a single contaminant problem with the different processes and to determine the most viable option. The limiting process data for the problem is given in Table C.1. It is assumed that the mass transfer is a linear function of concentration.

Table C.1 Limiting process data for Example 1

Process number	Mass load of contaminant (kg/hr)	Cin (ppm)	Cout (ppm)	Water flow rate (te/hr)
1	2	0	100	20
2	5	50	100	100
3	30	50	800	40
4	4	400	800	10

The minimum freshwater flowrate required for the system without reuse is found to be 112.5 te/hr. The minimum freshwater flowrate using reuse, regeneration reuse and regeneration reuse and regeneration recycle are calculated using the MATLAB codes no. B.1, B.2 and B.3 in Appendix B.

The data obtained is used to plot the limiting composite curve for the problem as shown below.

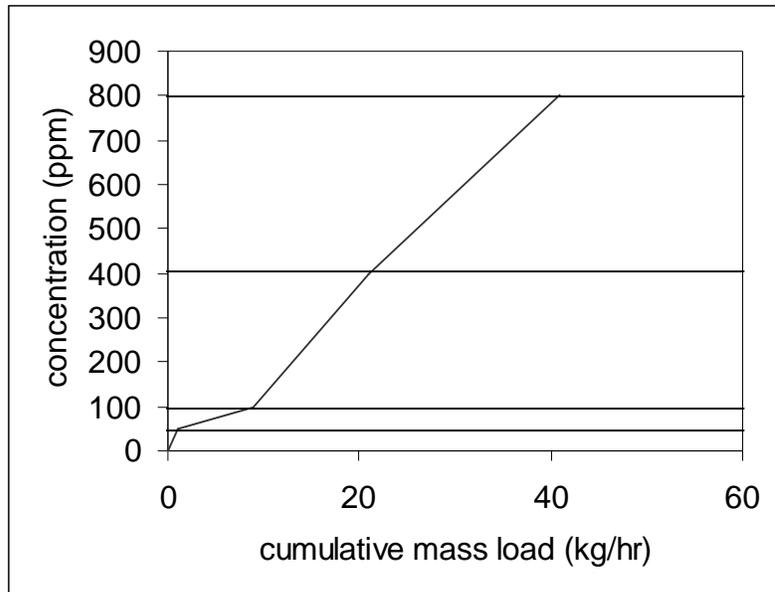


Figure C.1 Limiting composite curve for example 1

For the process of regeneration reuse and recycle an optimum regeneration outlet concentration of  $C_0 = 5$  ppm is specified.

### C.1.1 Results

#### 1. Reuse

For the determination of minimum freshwater flowrate with reuse, the following results are obtained,

Concentration intervals  $C(\text{ppm}) = [0 \ 50 \ 100 \ 400 \ 800]$

Mass load of contaminant in each interval =  $[1 \ 8 \ 12 \ 20]$

Cumulative mass load in each interval =  $[0 \ 1 \ 9 \ 21 \ 41]$

Flow rate in each interval =  $[0 \ 20 \ 90 \ 52 \ 51.25]$

The minimum freshwater flowrate required by reuse is found to be 90 te/hr

$$f_{min} = 90 \text{ te/hr}$$

#### 2. Regeneration reuse

Regeneration outlet concentration = 5 ppm

Minimum freshwater flowrate required without regeneration = 90 te/hr

Pinch concentration = 100 ppm

Minimum freshwater required after regeneration = 46.2 te/hr

Outlet concentration of wastewater = 793.3 ppm

$f_{min} = 46.2$  te/hr

### 3. Regeneration recycle

Regeneration outlet concentration = 5 ppm

Freshwater pinch concentration = 100 ppm

Flowrate of regenerated water = 73.7 te/hr

Flowrate of recycled water = 93.7 te/hr

Minimum freshwater flowrate required after recycle = 20 te/hr

### C.1.2 Analysis of Results

Table C.2 Freshwater Requirement by different processes for example 1

Process	Freshwater flowrate required (te/hr)	% reduction
Without reuse	112.5	
Reuse	90	20
Regeneration reuse	46.2	60
Regeneration recycle	20	82

### C.1.3 Discussion

The results obtained by the method of mathematical programming are found to be consistent with those obtained by Wang and Smith by the analytical methods. Hence, the mathematical programming approach can be used for the optimization of a given problem. There is a significant decrease in the quantity of freshwater required with reuse,

regeneration reuse and regeneration recycle as compared to systems without reuse options.

#### C.1.4 Conclusion

The process of regeneration recycle gives a maximum % reduction of 82 % in the freshwater requirement over that of the system without reuse. Hence, the process of regeneration recycle should be put into use while designing the network.

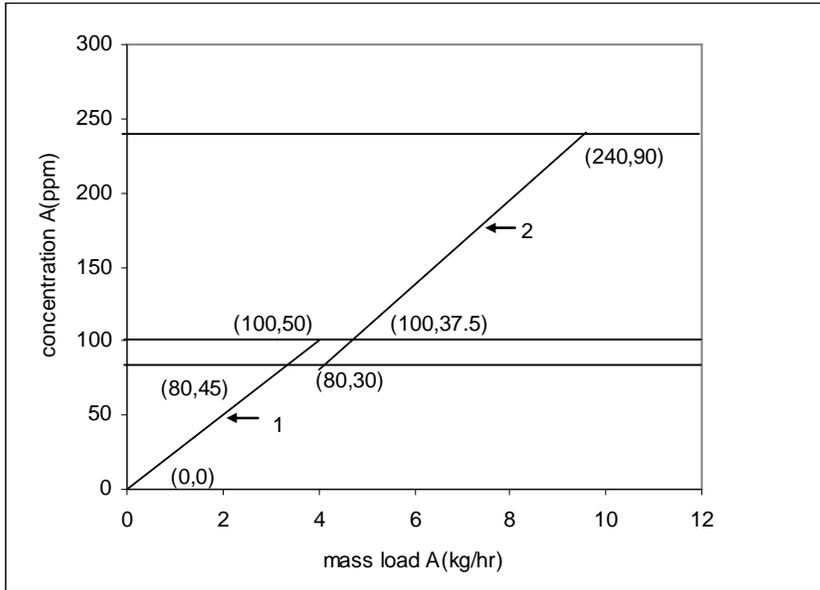
#### C.2 Example 2: Multiple Contaminants Problem

The limiting process data for the problem is taken from Wang and Smith (1994). The first step in the solution to the problem is the plotting of final composite curve in accordance to the principles of concentration shift presented by Wang and Smith (1994).

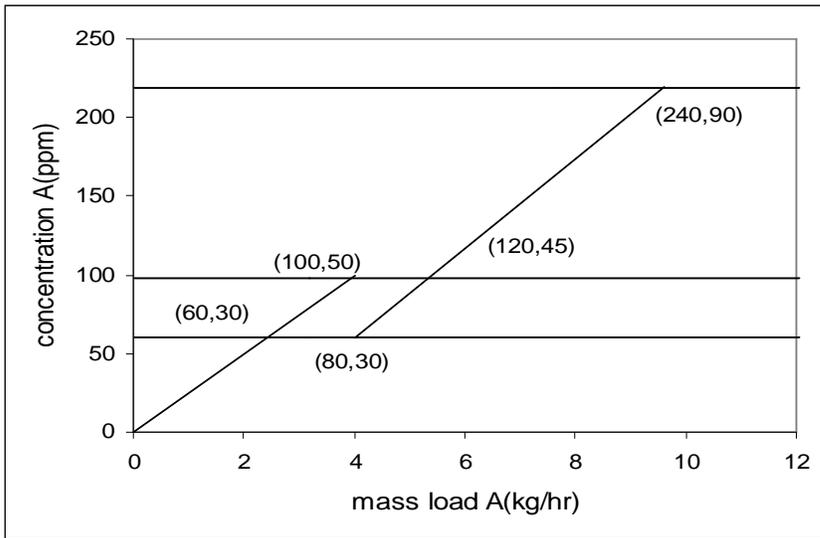
Table C.3 Limiting Process Data for Example 2

Process number	Contaminant	Mass load of contaminant (kg/hr)	$C_{in}$ (ppm)	$C_{out}$ (ppm)	Water flowrate (te/hr)
1	A	4	0	100	40
	B	2	25	75	
2	A	5.6	80	240	35
	B	2.1	30	90	

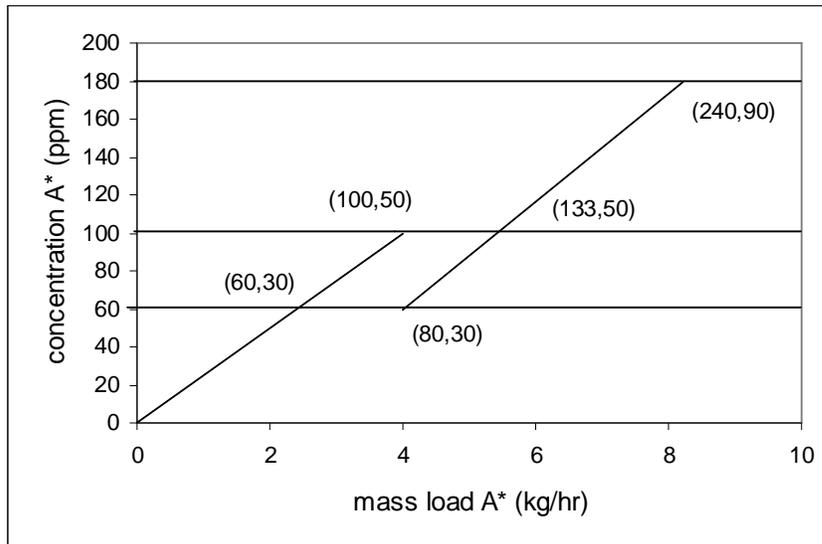
The limiting process data is used to plot the limiting water profiles followed by inlet and outlet concentration shifts to get the final limiting profile.



(a) Limiting water profile for example 2



(b) Limiting water profile after inlet concentration shift



(c) Limiting water profile after outlet concentration shift

Figure C.5 Limiting water profiles for example 2

The data obtained from the final limiting water profile after concentration shift is passed as an input to the code B.1 for single contaminant problem.

Input:

$C_{in} = [0 \ 60]$

$C_{out} = [100 \ 180]$

$f_{lim} = [40 \ 35]$

$m = [4 \ 8.2]$

Output:

$C = [0 \ 60 \ 100 \ 180]$

$m_l = [2.4 \ 3 \ 2.8]$

$cm = [0 \ 2.4 \ 5.4 \ 8.2]$

$f = [0 \ 40 \ 54 \ 45.6]$

$f_{min} = 54$

The minimum freshwater flowrate required for the multiple contaminant system is found to be 54 te/hr. This is consistent with the result obtained by Wang and Smith (1994) by analytical methods. Hence multiple contaminant systems can be analysed using computer programming with desired accuracy.

The output data is used to plot the limiting composite curve for the system as shown in Fig C.6.

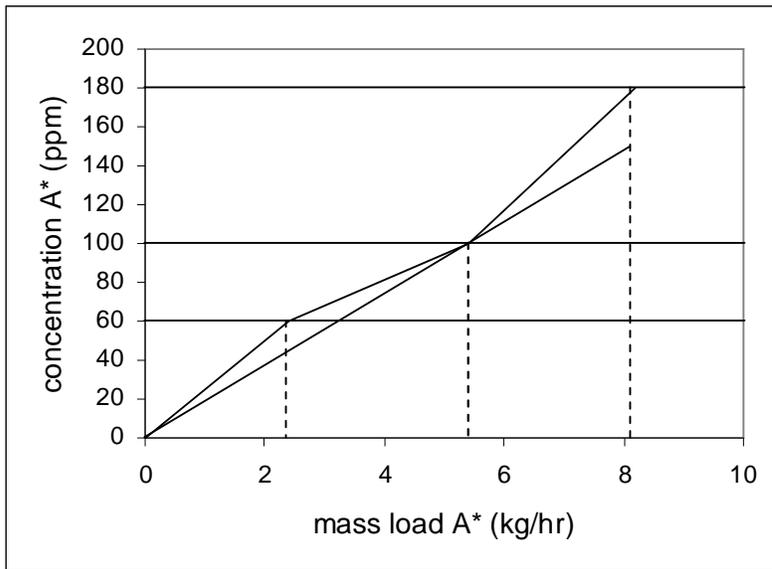


Figure C.6 Limiting composite curve for example 2