CHAPTER II
LITERATURE REVIEW

Water is the main resource in petrochemical plant, which is consumed by many process units such as extraction, absorption or distillation with steam. Wastewater generated at the end of process contains substances called “contaminants” from each unit. For example, in cooling unit, water is used as a cooling stream that comes out with some substance from fouling situation. Because of wastewater discharge regulation, treatment unit is used for wastewater treatment and it costs from amount of wastewater treated much more expensive than freshwater usage cost. In existing industrial complexes the water is usually fed to processes in a parallel arrangement to each water-using process, as shown in Fig. 2.1. Next, water streams from processes are mixed and sent to a central treatment station. Neither water reuse nor regeneration is applied.

Water minimization helps reduce treatment operating cost. Wastewater is reduced if the process decrease amount of freshwater usage by water allocation technique that will lead to Water Network design. Three main types of water network design are reuse, regeneration reuse and regeneration recycle (Wang *et al.*, 1994) as shown in Fig. 2.2.

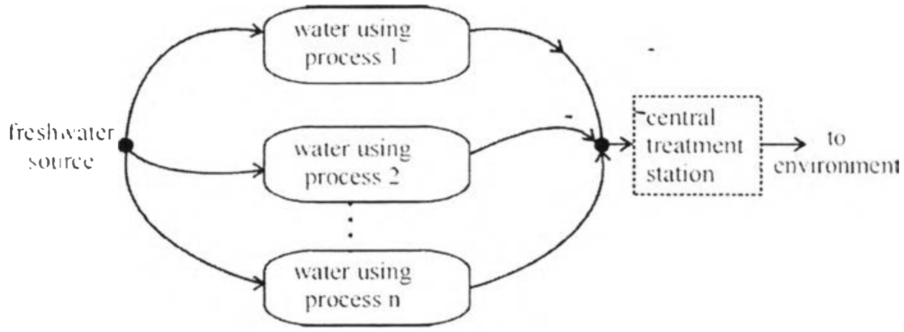

Figure 2.1 Traditional water network without minimization (Sieniutycz *et al.*, 2009).

2.1 Types of water-network design for minimization of fresh water usage

2.1.1 Reuse type

For this design, wastewater from one process or operation can be re-used directly in the next process without process interfering. Reuse type can reuse wastewater from other operations and/or use fresh water as shown in Fig. 2.2a. (Note that there may be recycling within an individual operation but here we consider only the net input and output from operations). This type requires a few steps to design that covered in simple mass balance. Due to the limitation of reuse stream contaminant, ability to reduce freshwater is lower than other types.

2.1.2 Regeneration reuse type

For this design, wastewater can be cleaned by treatment called regeneration to remove the contaminants, and then re-used in another operations. Reuse-after-regeneration stream can be blended with wastewater from other operations and/or freshwater shown in Fig. 2.2b. Let us emphasize that when water is reused after regeneration, in this case it does not re-enter processes in which it has previously been used. Despite amount of freshwater will reduce more, treatment unit will costing than reuse type.

2.1.3 Regeneration recycle type

For this design, wastewater is regenerated to remove contaminants and regenerated stream is recycled back to blend with stream entering the operation, as shown in Fig. 2.2c. Reuse-type water network designed by water composite curve (WCC) can be modified by adding regeneration unit to save more freshwater and reduce waste water (Kuo et al., 1997). This type is another probability to reduce freshwater by considering recycling of the same process.

Water-reuse type network is applied to improve the existing processes in order to substantially reduce freshwater consumption. This is often referred to as the water-reuse network. Reuse scheme is a simple method to reduce freshwater and wastewater which is first proposed in 1994 by Wang and Smith (Wang et al., 1994) targeting minimum freshwater requires graphical method called "Limiting Composite Curve (LCC)" which is based on Pinch technology (Linnhoff et al., 1983).

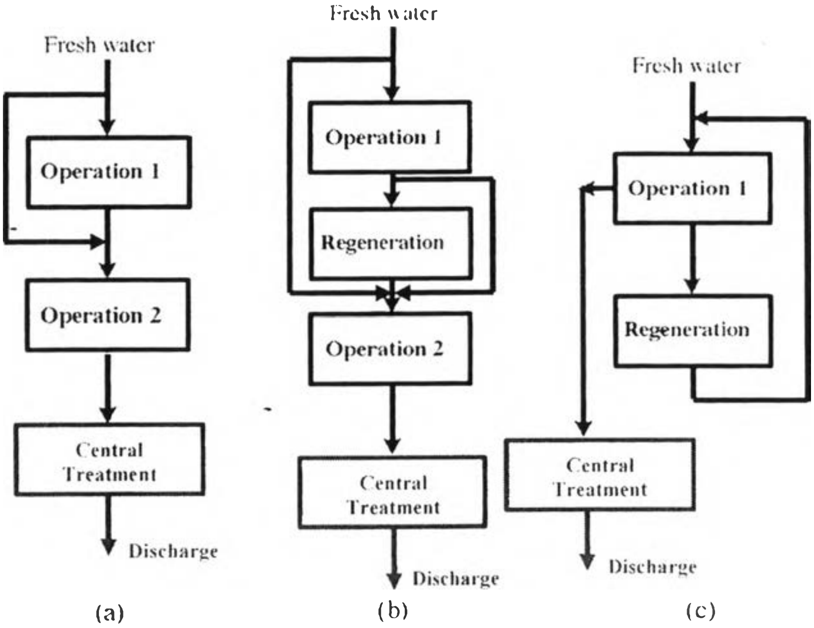

Figure 2.2 Water network types for fresh water minimization
(a) Reuse, (b) Regeneration reuse, and (c) Regeneration- recycle (Relvas *et al.*, 2008).

There are numerous techniques based on conceptual design and mathematical optimized design where the main purpose

is to find minimum amount of freshwater required and minimum wastewater discharge accompanied with water network design to reduce either freshwater cost or wastewater treatment cost.

2.2 Data for water network design

Data for water network design to minimize freshwater depend on known parameters of process which is divided into two main types, fixed-load problem and fixed-flowrate problem.

2.2.1 Fixed-load problem

All water using processes are modeled as mass transfer operation (e.g., washing, scrubbing, and extraction) with water being used as only mass separating agent. Each operation has a fixed contaminant load. The inlet and outlet contaminant concentration are constricted to not over the allowable limitation values which follow the mass balance equation (Eq. 2.1). Stream flowrate is variable that will satisfy contaminant mass load. Eq. 2.2 and 2.3 are inequality constraints for Eq. 2.1.

$$\Delta m = F(C_{out} - C_{in}) \tag{2.1}$$

$$C_{in} \leq C_{in}^{\max} \tag{2.2}$$

$$C_{out} \leq C_{out}^{\max} \tag{2.3}$$

Where Δm is Contaminant mass load

F is Stream flowrate

C_{out} is Outlet contaminant concentration

C_{in} is Inlet contaminant concentration

$C_{out}^{\max}$ is Maximum outlet contaminant concentration

$C_{in}^{\max}$ is Maximum inlet contaminant concentration

This type of design is first considered as water network design for freshwater minimization (Wang *et al.*, 1994). There are many papers (Olesen *et al.*, 1997, Bagajewicz *et al.*, 2001, Dunn *et al.*, 2001) similar to this problem. Recently, water and heat exchanger networks are designed by mathematical programming technique using fixed-load problem data and additional temperature data from each operation. There are many papers relating to this study done by (Bagajewicz *et al.*, 2002, Bogataj *et al.*, 2008, Dong *et al.*, 2008, Leewongtanawit *et al.*, 2009, Liao *et al.*, 2011, Martinez-Patiño *et al.*, 2012, Ahmetović *et al.*, 2013).

2.2.2 Fixed-flowrate problem

The unit operations for this design problem are quantity controlled, for example, water-using units like boilers, cooling towers and reactors that do not involve mass transfer. The units have fixed inlet and outlet flowrates, and they may not be equal because of water losses or gains. The outlet streams always leave the operations at the maximum concentrations, while the inlet streams enter the operations with concentration less than maximum values. Fixed-flowrate problem were first proposed in 1996 (Dhole et al., 1996) that all the inlet streams be regarded as sinks or demands and outlet streams be regarded as sources. This allows each has many sinks and sources to be considered which represented in Fig. 2.3. Compared to heat exchanger pinch technology, sink and source are analogous to cold and hot streams, respectively. There are many techniques to target minimum freshwater required and minimum wastewater discharged in process from fixed flowrate data. Source-sink mapping diagram (El-Halwagi et al., 1996) was introduced by plotting flowrate or species mass load on horizontal axis and composition on vertical axis Where sources and sinks are plotted as two lines on this diagram, it can be used to determine direct recycle opportunities. Two graphical techniques were proposed as Water Surplus Diagram (Hallale, 2002) and Water Composite Curve (WCC) (El-Halwagi et al., 2003, Prakash et al., 2005a). Water Surplus Diagram is similar to grand composite curve of heat exchanger synthesis pinch technology (Linnhoff et al., 1983).

Source and sink concentration and flowrate are plotted together on water purity vs. flowrate diagram, but it requires a tedious iterative procedure to generate. Water Composite Curve similar to composite curve of heat exchanger network synthesis is non-iterative procedure to target minimum freshwater sources and sinks composite are plotted separately, minimum freshwater can be targeted by shifting source composite to pinch point. Extended from graphical methods, Water Cascade Analysis (Manan et al., 2004, Foo, 2008) is a cascading problem table algorithm procedure identifying minimum freshwater and minimum wastewater in exactly values with more accuracy than graphical methods. This technique can solve threshold problem with zero freshwater requires and/or zero wastewater discharged.

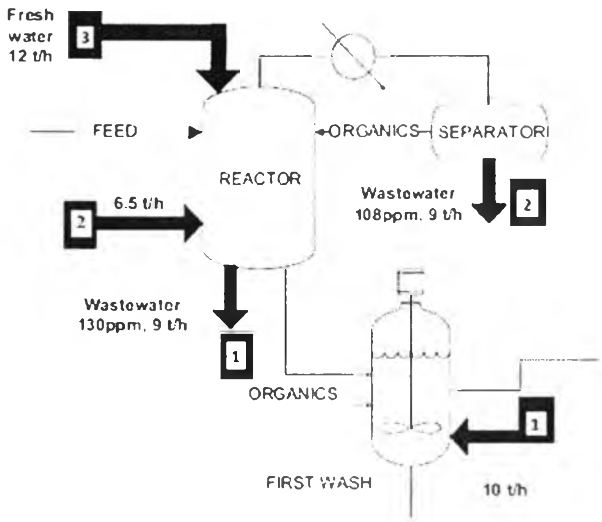

Figure 2.3 Sources (outlet streams) and sinks (inlet streams) representation (Foo, 2008).

2.3 Freshwater targeting and water network design

The first water minimization was introduced in 1980 (Takama *et al.*, 1980). They formulate an optimal water allocation problem that includes both water- using unit and wastewater treatment unit in petrochemical refinery by employ a superstructure optimization approach to cope with the problem. A substantial knowledge of water network design is later proposed in 1994 (Wang *et al.*, 1994) by two steps method that is targeting and design for fixed load problem. Mathematical programming is give more achievement in this area that has more power to solve complex problems (Bagajewicz, 2000). For fixed flowrate problem, pinch technology is mainly used to solve this problem (Prakash *et al.*, 2005a, Foo, 2008). There are two categories of water network design consist of insight-based methods and optimization-based methods (Smith, 2005).

2.3.1 Insight-based methods

2.3.1.1 *Fixed-load water network*

Similar to heat exchanger network (HEN) design methods, procedure approach to design water network (WN) using water pinch concept is widely used. Typically, development of water network consists of two main steps, targeting and design. The water pinch targeting method for water-using processes of mass transfer type (fixed load problem) will be described by Example 1 which shown in Table 1 taken from Wang and Smith (Wang *et al.*, 1994). For each process the mass loads of the contaminant and the maximum values of inlet and outlet concentrations in water streams are given in the table. It is assumed that there is a single freshwater source with contaminant concentration is zero ppm (parts per million).

Table 2.1 Water-using processes for Example 1 (Wang *et al.*, 1994)

Process number	**1**	**2**	**3**	**4**
Contaminant mass load, Δm_p (ton/h)	2	5	30	4
Maximum inlet concentration, $C_p^{in,\max}$ (ppm)	0	50	50	400
Maximum outlet concentration, C_p^{out} (ppm)	100	100	800	800

Total freshwater usage can be calculated for a parallel arrangement as shown in Fig. 2.4. For each process (p=1, 2, 3, 4) in the parallel network the minimum flowrate of freshwater calculated by mass balance (Eq.2.4).

$$F_p = \frac{\Delta m_p}{C_p^{out} - C_0} \tag{2.4}$$

Where C_0 is freshwater concentration which is zero ppm. For Example 1 the values of freshwater flowrate are 20, 50, 37.5 and 5 t/h, respectively. The total flowrate without reuse or minimization is thus 112.5 t/h. In the water pinch approach, similar to heat pinch methods, the total range of contaminant concentration in the data is divided into intervals. The bounds of an interval correspond to the maximum inlet and the maximum outlet concentration of each process.

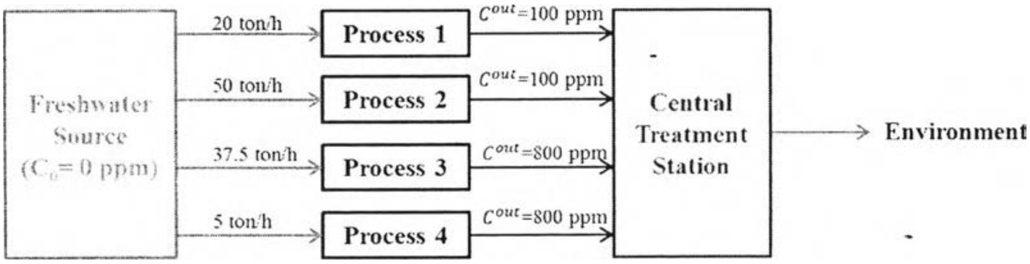

Figure 2.4 Process diagram of Example 1 with four water-using process.

Limiting Composite Curve (LCC) which is concentration vs. cumulative mass load is constructed to targeting minimum freshwater by these steps. Each operation mass loads are put in concentration intervals in linear line as shown in Fig. 2.5a. This would have created additional intervals at the points of intersection of the segments by combining operations within concentration intervals to limiting composite curve in Fig. 2.5b that represent the total system to single water-using operation.

Zero concentration is rotate counter clockwise until it touches the composite curve. The first point that is touched is a pinch point of process. Minimum freshwater flowrate is calculated by reciprocal of slope which is reduced from 112.5 t/h to 90 t/h. The contaminant concentration of the limiting composite curve must not be lower than one from the water supply line and the latter cannot cross the limiting composite curve. The way of constructing water supply line ensures that contaminant concentration in water streams of processed is not higher than given maximal values (Eq. 2.2 and Eq. 2.3).

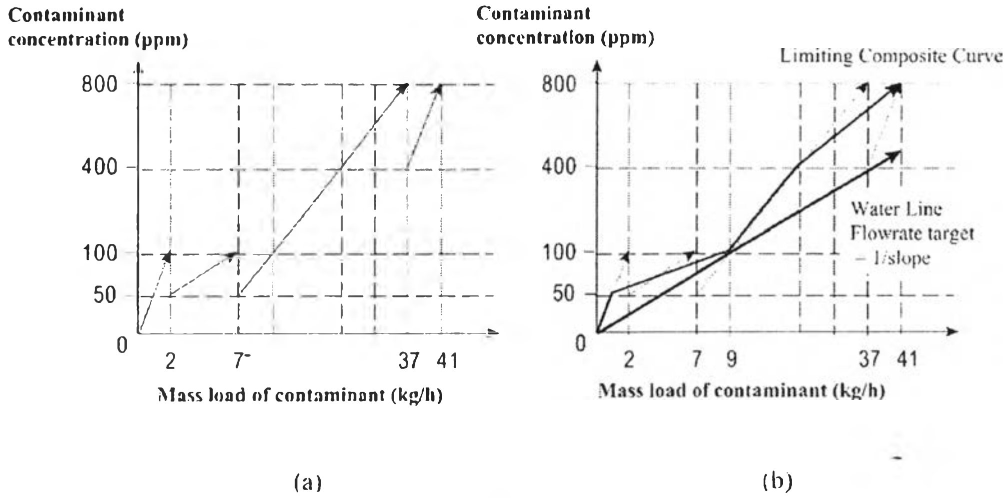

Figure 2.5 Limiting Composite Curve for Example 1 (a) Constructed, (b) Combined (Hallale, 2002).

To design water network after targeting minimum freshwater, they proposed two terms, maximum driving forces and minimum number of water sources obtain from primal HEN design procedure (Linnhoff *et al.*, 1983). Water network is constructed in grid design as shown in Fig. 2.6b, and conventional network shows in Fig. 2.6c. This kind of grid design contains splitting and mixing in processes which is difficult for practical operation. To overcome this, they proposed loop breaking technique which eliminates by passing and mixing. Fig. 2.7 shows the loop breaking procedure and the final result. This method is a conservative technique that difficult to implement with large system.

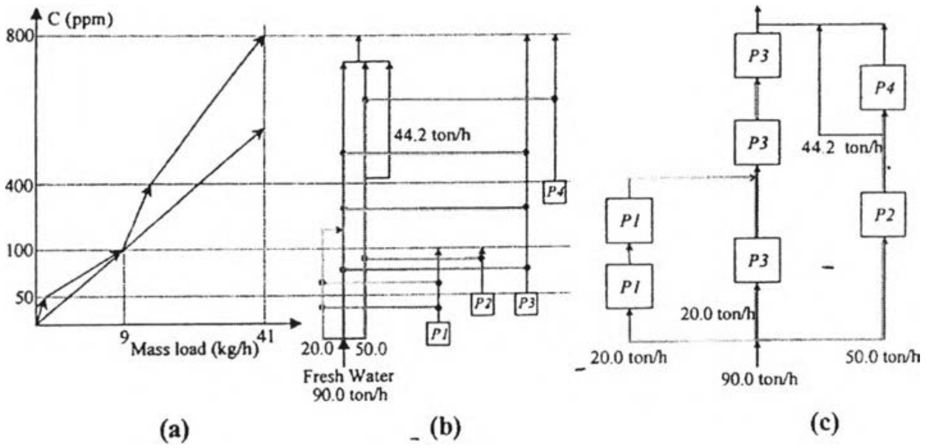

Figure 2.6 Network design grid procedure (a) Limiting composite curve, (b) Design grid, and (c) Conventional network (Wang *et al.*, 1994).

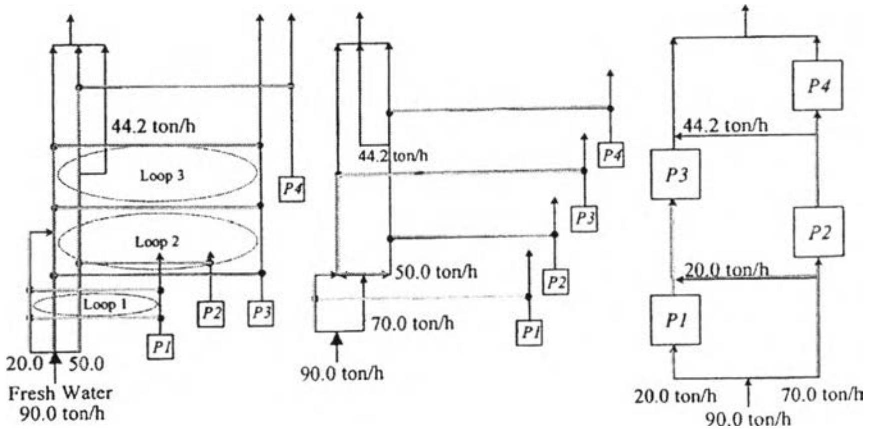

Figure 2.7 Loop breaking for final water network (Wang *et al.*, 1994).

Many different types of regeneration processes can be used to improve quality of wastewater as shown in Fig. 2.8, e.g. gravity settling, filtration, membranes, activated carbon, biological treatment, etc. Two general criteria are common used to specify the performance of regeneration process as show in Eq. 2.5 and Eq. 2.6

$$C^{out} \leq C^{in} \tag{2.5}$$

$$R = \frac{F^{in}C^{in} - F^{out}C^{out}}{F^{in}C^{in}} \tag{2.6}$$

Where R is recovery ratio of regeneration process.

Only slight modifications are necessary to determine the minimum freshwater flowrate for regeneration with reuse from the limiting composite curve plot. The composite curve of water supply line is changed to stepwise segmented strainght lines; before-and-after regeneration lines, as shown in Fig. 2.8. Wang and Smith (Wang *et al.*, 1994) later proved that to minimize freshwater flowrate, contaminant concentration of the inlet to regeneration process (C^{reg}) has to satisfy the condition (Eq. 2.7)

$$C^{reg} \geq C^{Pinch} \tag{2.7}$$

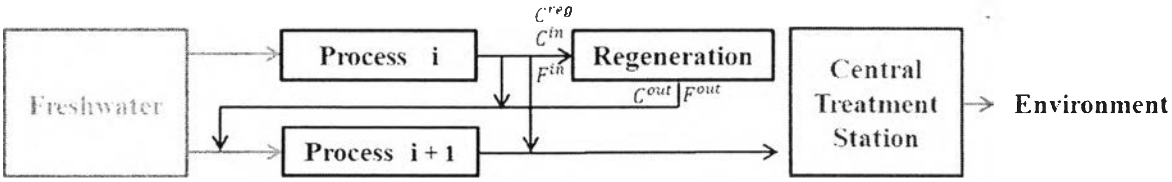

Figure 2.8 Scheme of regeneration process.

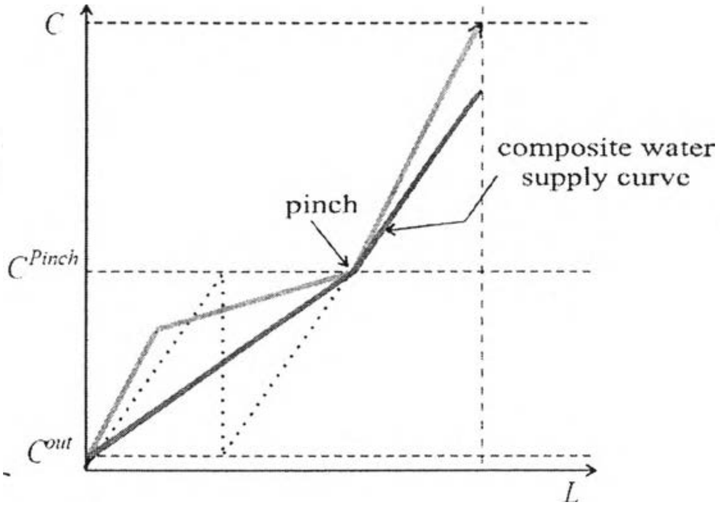

Figure 2.9 Construction of Composite Water Supply Curve (Sieniutycz *et al.*, 2009)

Notice that pinch concentration (C^{Pinch}) corresponds to the concentration at the pinch calculated for water reuse only. The inequality should be taken as equality in order to minimize wastewater flowrate. Fig. 2.9 illustrates the construction of composite water supply line for data of Example 1 for a regeneration process with fixed outlet concentration. At first, dotted lines are drawn for water before and after regeneration and then the solid composite curve are made from them according to the rules for constructing composite curve shown in Fig. 2.5. Notice that both dotted lines have to lie in parallel since flowrate before and after regeneration is identical.

This construction is valid for regeneration without recycling the freshwater flowrate drops to 46.2 t/h, for Example 1. Regeneration with recycling further reduces the freshwater usage since the composite water supply curve has its starting point below the outlet concentration from regeneration (C^{out}).

2.3.1.2 *Fixed-flowrate water network*

For fixed flowrate problem, Water Composite Curve is proposed in 2005 (Prakash *et al.*, 2005a) extended from Dhole's work (Dhole *et al.*, 1996). This is visualized graphical method to represent minimum freshwater require and wastewater discharge. The source (wastewater outlet) and sink (freshwater inlet) data used to illustrate this technique are shown in Table 2.2 for Example 2. Each source and sink contaminant load are calculated by Eq. 2.1. And then, cumulative flowrate and contaminant load are found separately for source and sink are calculated for composite curve as shown in Table 2.2. From this example 2, the base case requires overall freshwater flowrate of 300 ton/hr and overall wastewater flowrate of 280 t/h.

Table 2.2 Sinks and sources data for Example 2 (Prakash *et al.*, 2005a)

	Contaminant concentration (ppm)	**Flowrate (t/h)**	**Contaminant load (kg/s)**	**Cumulative flowrate (t/h)**	**Cumulative load (kg/s)**
Sinks					
1	20	50	1	50	1
2	50	100	5	150	6
3	100	80	8	230	14
4	200	70	14	300	28
Sources					
Freshwater	0	0	0	0	0
1	50	50	2.5	50	2.5
2	100	100	10	150	12.5
3	150	70	10.5	220	23
4	250	60	15	280	38

The graph consists of source and sink composite curves where cumulative flowrate on x-axis and cumulative contaminant load on y-axis. Usually, source contaminant load must be less than or equal to sink composite at every point as shown in Fig. 2.10a. To overcome the results, source composite should be shifted horizontally to right till it below the sink composite. Such a shift implies an increase of flowrate without any increase of contaminant load. Pinch point of process is located at the touch point of source and sink composite that meaning to minimum driving force of difference concentration between source and sink. Minimum freshwater flowrate and wastewater flowrate are targeted by source and sink composite interval at below and above pinch which freshwater and wastewater are reduced to 70 and 50 t/h respectively as shown in Fig. 2.10b.

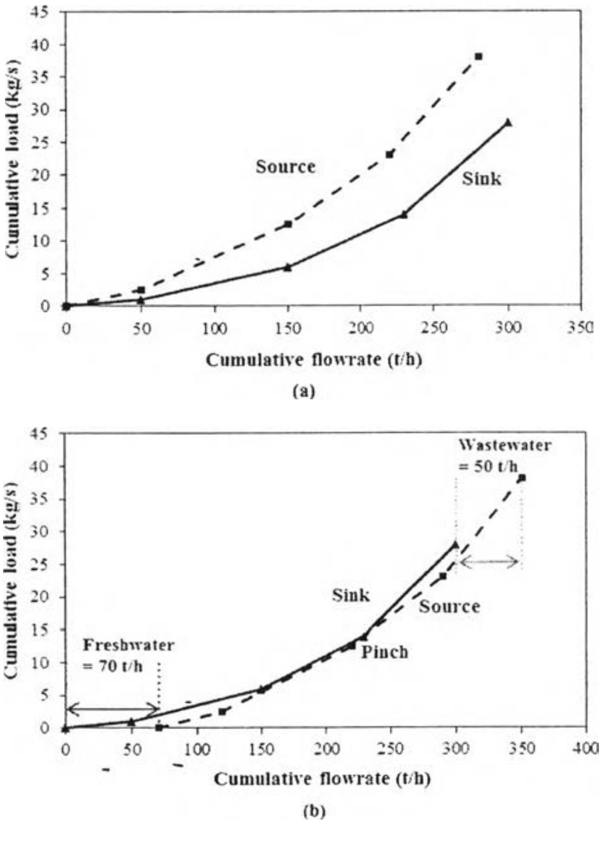

Figure 2.10 Water Composite Curve for Example 2 (a) Before source shift and (b) After source shift.

Later in 2004, the other technique is proposed which is "Water Cascade Analysis (WCA)" (Manan *et al.*, 2004, Foo, 2008). WCA is a well-established algebraic technique. The technique can be used to determine various targets for direct reuse/recycle, for both single and multiple freshwater resources (fixed flowrate problems). WCA technique is also useful for situations that water network either require fresh water without wastewater generation, or on the other extreme generate wastewater without any fresh water intake which call "Threshold problems"(Foo, 2008).

The first step in conducting a WCA is to locate the various water sink (inlet stream) and source (outlet stream) at their respective concentration levels. As shown in the first two column of Water Cascade Table (WCA), which show in Table 2.3, the concentration level (C_k) are arranged in an ascending order (k=1, 2, ..., n), and the flowrates of water sink or demand (F_j) and source (F_i) are assumed at their respective concentration level k in column 3 and 4. Column 5 represents the net flowrate, ($\sum F_i - \sum F_j$) between water sources and sinks at each concentration level k; with positive indicating surplus, negative indicating deficit.

Next, the net water flowrate surplus/deficit is cascaded down the concentration levels, to yield the cumulative surplus/deficit flowrate ($F_{c,k}$) in column 6 with an assumed zero fresh water flowrate ($F_{FW}=0$). This assumed is to facilitate the search for the minimum fresh water. The next step involves setting up the cumulative impurity load cascade (Cum.Δm) to fulfill the load constraint. Impurity load in column 7 (Δm_k) is obtained by the product of cumulative flowrate ($F_{c,k}$) and the concentration difference across two subsequent concentration level ($C_{k+1}-C_k$). Cascading the impurity load down the concentration levels of column 8 yields the cumulative load (Cum.Δmk). In such case, an interval fresh water flowrate ($F_{FW,k}$,column 9) is calculated by dividing Cum.Δm_k by the concentration difference between level k (C_k) and the fresh water concentration (C_{FW}) shown in Eq. 2.8.

$$F_{FW,k} = \frac{Cum.\Delta m_k}{C_k - C_{FW}} \tag{2.8}$$

The absolute value of the largest negative $F_{FW,k}$ will then replace the earlier assumed zero fresh water flowrate in the flowrate targeting (column 6) to obtain a new set of feasible flowrate cascade and hence feasible load cascade.

Table 2.3 Water Cascade Table for water flowrate targeting

k	C_k	F_j	F_i	F_i-F_j	FC_k	Δm_k	Cum.Δm_k	FW_k
					F_{FW}			
1	C_1	F_{j1}	F_{i1}	F_{i1}-F_{j1}	-			
					FC_1	Δm_1		
2	C_2	F_{j2}	F_{i2}	F_{i2}-F_{j2}			Cum.Δm_2	FW_1
					FC_2	Δm_2		
3	C_3	F_{j3}	F_{i3}	F_{i3}-F_{j3}			Cum.Δm_3	FW_3
					FC_3	Δm_3	.	.
4	C_4	F_{j4}	F_{i4}	F_{i4}-F_{j4}	.	.	.	.
.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	Cum.Δm_{n-1}	FW_{n-1}
.	.	.	.	.	FC_{n-1}	Δm_{n-1}		
n	C_n	F_{jn}	F_{in}	F_{in}-F_{jn}			Cum.Δm_n	FW_n

Example 2 is used to illustrate this technique. Table 2.4 show that the assumption of zero freshwater flowrate ($F_{FW} = 0$), then the highest deficit $F_{FW,k}$ is -70 t/h which indicate to minimum freshwater of process. Table 2.5 show that 70 t/h of fresh water can fulfill the highest deficit by replace initial zero freshwater flowrate assumption. The last row value in column 6 is minimum wastewater flowrate. Zero value instead of largest deficit $F_{FW,k}$ is water pinch point of the process. This technique gives the same result as Water Composite Curve but use less steps to target minimum freshwater and show more exact result value.

Table 2.4 Water Cascade Table for Example 2 (F_{FW} = 0 t/h)

k	C_k	F_j	F_i	F_i-F_j	FC_k	Δm_k	Cum.Δm_k	FW_k
					0			
1	0			0				
					0	0		
2	20	50		-50			-0	0
					-50	-1500		
3	50	100	50	-50			-1500	-30
					-100	-5000		
4	100	80	100	20			-6500	-65
					-80	-4000		
5	150		70	70			-10500	**-70**
					-10	-500		
6	200	70	60	-10			-11000	-55
					-20	-19996000		
7	1000000			0			539227421	539.227

Table 2.5 Water Cascade Table for Example 2 (F_{FW} = 70 t/h)

k	C_k	F_j	F_i	F_i-F_j	FC_k	Δm_k	Cum.Δm_k	FW_k
					70			
1	0			0				
					70	1400		
2	20	50		-50			1400	70
					20	600		
3	50	100	50	-50			2000	40
					-30	-1500		
4	100	80	100	20			500	5
					-10	-500		
5	150		70	70			0	**0**
					60	3000		
6	200	70	60	-10			3000	15
					50	49990000		
7	1000000			0			539227421	539.227

To design the water network after minimum freshwater flowrate is targeted, they generate by the "Nearest Neighbors Algorithm (NNA)" principal. It states to satisfy a particular water sink flowrate and contaminant constraint, the source streams to be chosen are the nearest available neighbors to the sink in terms of contaminant concentration (Prakash *et al.*, 2005b). For example, Sink 1 which that must has concentration less than or equal to 20 ppm with 20 t/h of flowrate is satisfied by sources that has nearest concentration (Freshwater and Source 1). 30 t/h of Freshwater and 20 t/h of Source one are combined to generate 50 t/h of Sink 1 which combined concentration is equal to 20 ppm that not over the sink 1 concentration constraint. Fig. 2.11 shows the final water network after applied this principal.

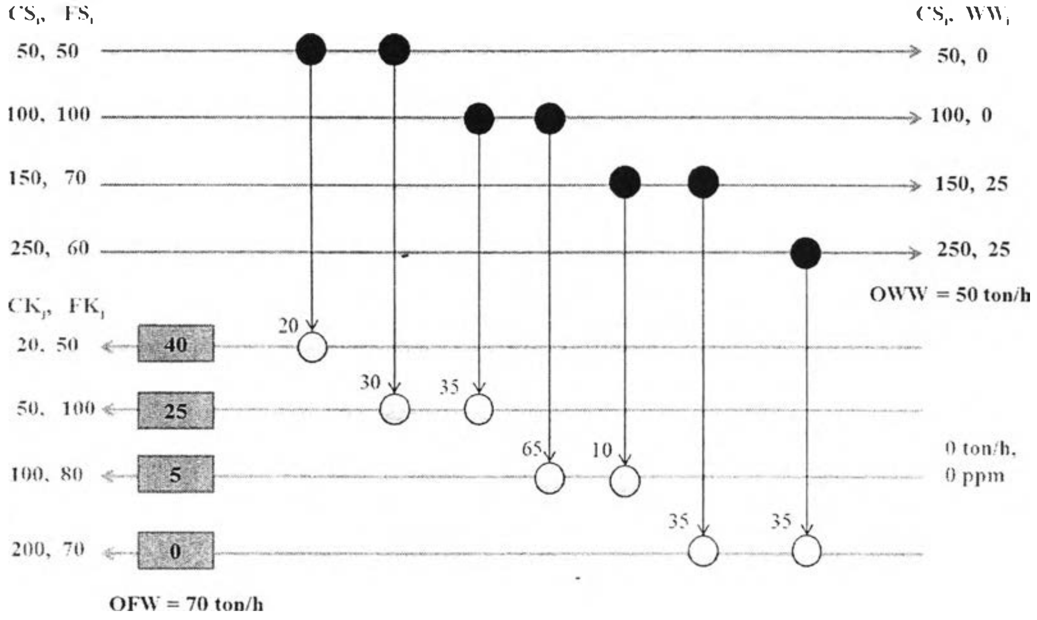

Figure 2.11 Water network for Example 2 by NNA principal (Prakash *et al.*, 2005a) shown in grid diagram.

2.3.2 Optimization-based methods

The mathematical programming generally involves with designing, integration and operation of water network synthesis problem. It consists of three major steps; 1) development of water network model, 2) formulation of a mathematical program that generally involves discrete and continuous variables, and 3) the solution of the optimization model.

Mathematical programming techniques have been considered since the last decade. For instance, the solution of mixed-integer nonlinear programming problems and the rigorous global optimization of nonlinear programs has become a reality. Furthermore, there have been great advances in the capability of solving very large problems, particularly for linear and mixed-integer linear programming techniques.

To begin with discrete or continuous optimization problems, it relates to mixed-integer optimization problems that have the following form (Grossmann *et al.*, 2000);

Objective: $\text{Min } Z = f(x,y)$

Constraints: $h(x,y) = 0$

$g(x,y) \leq 0$

$x \in X, y \in (0,1)$

Where $f(x,y)$ is the objective function (e.g. freshwater flowrate), $h(x,y) = 0$ are the equations that describe the performance of the system (mass and heat balances, design equations), and $g(x,y) \leq 0$ are inequalities that define the specification or constraints for feasible options. The variables x are continuous and correspond to the state or design variables, while y are the discrete variables, which generally are restricted to take 0-1 values to define the selection of an item or an action.

Mixed-integer programming (MIP) corresponds to a mixed-integer nonlinear programming (MINLP) when any functions involved are nonlinear. If all functions are linear, it will correspond to a mixed-integer linear programming (MILP). If there no 0-1 variables, the problem of mixed-integer programming (MIP) reduces to a nonlinear programming (NLP) or linear programming (LP) depending on whether or not the function are linear.

The formulation and solution of major types of mathematical programming problems can be effectively performed with modeling system such as GAMS. The model must be expressed explicitly in algebraic form. Moreover, the advantage is automatically with codes for solving the various types of problems.

For fixed load problems, the most technique that optimally target the minimum fresh water is developed in linear programming (Savelski *et al.*, 2000, Bagajewicz *et al.*, 2001). They generated the model for water-using/water-disposing process. It is desired to determine a network of interconnections of water streams among the processes so that the overall fresh water consumption is minimized while the processes receive water of adequate quality. This is what is referred to as the Water/Wastewater Allocation Planning (WAP) problem.

Fig. 2.12 illustrates schematically the way these processes are aligned. The set of fresh water users consists of the set H and subsets of sets I and T. Similarly, the set of wastewater users is formed by a subset of I and a subset of T. That is, not all intermediate and terminal processes use fresh water and/or are solely fed by wastewater.

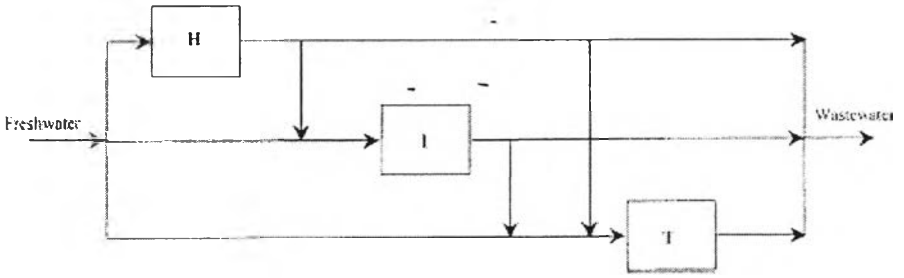

Figure 2.12 Schematic representation of a water network (Bagajewicz *et al.*, 2001).

Fig. 2.13 shows the concept of a set of precursors and a set of receivers. Set of precursors (P_j) of a process j: A set of precursors of a process is the set of all processes that send wastewater to process j. Set of receivers (R_j) of process j: A set of receivers of a process is the set of all processes where wastewater from process j is sent.

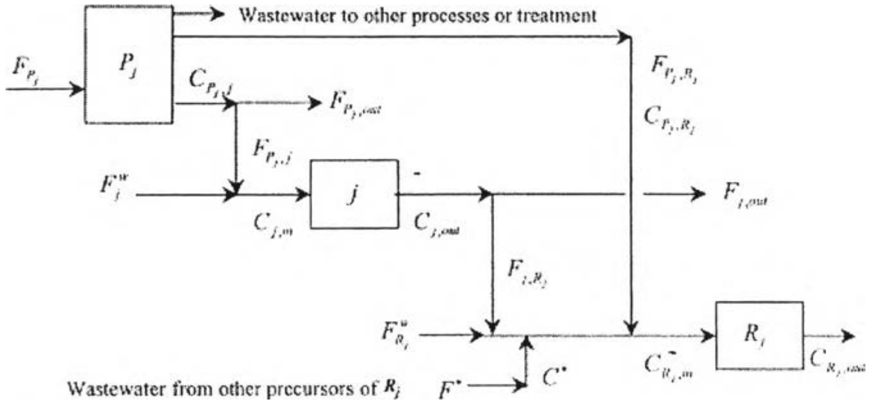

Figure 2.13 Precursors and Receivers of process j (Bagajewicz *et al.*, 2001).

After that, they showed that the model for single component can be linearized by the following necessary conditions (Bagajewicz, 2000).

Condition 1, Maximum outlet concentrations: If a solution of the water allocation problem is optimal then all fresh water-using processes reach their maximum possible outlet concentration. Degenerate solutions with lower outlet concentrations but the same overall freshwater consumption may exist. However, these degenerate solutions are such that the flow rate through some processes is larger. Thus, they are not preferred.

Condition 2, Concentration monotonicity: If a solution to the water allocation problem is optimal, then at every process, the outlet concentrations are not lower than the concentration of the combined wastewater stream coming from all the precursors. In other words, given a process j, then, $C_{i,out} \geq C_{Pi,i}$, where $C_{Pi,i}$ is the concentration of the combined wastewater of all the precursors. The non-linear programming (NLP) is shown below.

Objective function $\min \sum_{j} F_{j}^{w}$

Constraints

$$F_{j}^{w} + \sum_{i} F_{i,j} - \sum_{k} F_{j,k} - F_{j,out} = 0, \ \forall j \in N, i \in P_{j}, k \in R_{j}$$

$$F_{h}^{w} - \frac{L_{H}}{C_{h,out}^{\max}} = 0, \ \forall h \in H$$

$$\sum_{i} F_{i,j}(C_{i,out} - C_{j,in}) - F_{j}^{w} C_{j,in} = 0, \ \forall j \in \overline{H}, i \in P_{j}$$

$$\sum_{i} F_{i,j}(C_{i,out} - C_{out}) - F_{j}^{w} C_{j,out} + L_{j} = 0, \ \forall j \in \overline{H}, i \in P_{j}$$

$$C_{j} \leq C_{j}^{\max}, \ \forall j \in \overline{H}$$

$$C_{i} \leq C_{i}^{\max}, \ \forall i \in P_{i}$$

The previous NLP has bilinear terms in flowrate and concentration. These bilinearities can be eliminated using the necessary condition of maximum outlet concentrations, that is, setting outlet concentrations to their maximum values. The constraints can now be combined as follows.

$$\sum_{i} F_{i,j}(C_{i,out}^{\max} - C_{j,in}) - F_{j}^{w} C_{j,in} = 0$$

$$C_{j,in} = C_{j,in}^{\max}$$

The combined constraint is

$$\sum_{i} F_{i,j}(C_{i,out}^{\max} - C_{j,in}^{\max}) - F_{j}^{w} C_{j,in}^{\max} \leq 0, \ \forall j \in \overline{H}, i \in P_{j}$$

The resulting linear problem (LP) is

Objective function $\min \sum_{j} F_{j}^{w}$

Constraint

$$F_{j}^{w} + \sum_{i} F_{i,j} - \sum_{k} F_{j,k} - F_{j,out} = 0, \ \forall j \in N, i \in P_{j}, k \in R_{j}$$

$$F_h^w - \frac{L_H}{C_{h,out}^{\max}} = 0, \qquad \forall h \in H$$

$$\sum_i F_{i,j}(C_{i,out}^{\max} - C_{j,in}^{\max}) - F_j^w C_{j,in}^{\max} \leq 0, \ \forall j \in \overline{H}, i \in P_j$$

$$\sum_i F_{i,j}(C_{i,out}^{\max} - C_{j,out}^{\max}) - F_j^w C_{j,out}^{\max} + L_j = 0, \ \forall j \in \overline{H}, i \in P_j$$

$$Fi_{,j}; F_j^w; F_{j,out} \geq 0, \ \forall j \in N$$

From the above LP, the values of concentration now are fixed by maximum values that will change bilinear form of NLP to linear form. The easier problem can be solved by GAMS (Program that can solve large mathematical model) to get $\sum_j F_j^w$ (minimum fresh water).

On the other hand, the mathematical optimization approach for water network synthesis has also received much attention from the research community. The first published work of water allocation or water network is developed by industry itself more than twenty years ago (Takama *et al.*, 1980), They used mathematical programming to solve a refinery example. A superstructure of all water using operations and cleanup processes was set up and an optimization was then carried out to reduce the system structure by removing irrelevant and uneconomical connections. The model is transformed into a series of problems without inequality constraints by using a penalty function and finally solving it using the complex method. After that, mathematical model which is, non-linear problem procedure was represented (Huang *et al.*, 1999). The model called 'Superstructure model' for water usage and treatment unit (fixed load problem) which shown in Fig. 2.14 consist of mixer (M), splitter (S), operation (U) and treatment unit (T).

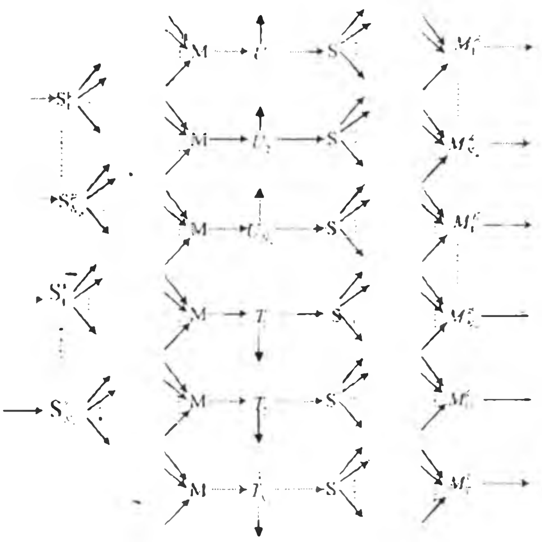

Figure 2.14 General superstructure model for water usage and treatment network (Huang *et al.*, 1999).

A good optimal water network which recently presented is based on Water/Wastewater Allocation Planning (WAP) problem which illustrated before in Fig. 2.13. They introduced mixed-integer linear programming (MILP) mathematical program to overcome optimal water networks. Once the target is obtained different network alternatives can be sought. To do that, different objective functions are proposed and the minimum fresh water usage is added as a constraint. These objective functions are minimum number of interconnections, minimum fixed cost of interconnections, compulsory/forbidden match (Bagajewicz *et al.*, 2001). We now consider the case of minimum number of interconnections. Consider the following constraint:

$$F_{i,j} - UY_{i,j} \leq 0, \quad \forall j \in \overline{H}, i \in P_l$$

This relates the inter-processes flowrates with the integer variables. In these constraints, U is a number larger than any feasible value of $F_{i,j}$ $(\forall i, j)$. For this problem, the value of U was chosen to be larger than the targeted fresh water flowrate (α). In turn, the targeting constraint is

$$\sum_j F_j^w = \alpha$$

Thus, the MILP model is

Objective function $\quad \min \sum_j F_j^w$

Constraint

$$F_j^w + \sum_i F_{i,j} - \sum_k F_{j,k} - F_{j,out} = 0, \quad \forall j \in N, i \in P_j, k \in R_j$$

$$\sum_j F_j^w = \alpha$$

$$F_h^w - \frac{L_H}{C_{h,out}^{max}} = 0, \quad \forall h \in H$$

$$\sum_i F_{i,j}(C_{i,out}^{max} - C_{j,in}^{max}) - F_j^w C_{j,in}^{max} \le 0, \quad \forall j \in \overline{H}, i \in P_j$$

$$\sum_i F_{i,j}(C_{i,out}^{max} - C_{j,out}^{max}) - F_j^w C_{j,out}^{max} + L_j = 0, \quad \forall j \in \overline{H}, i \in P_j$$

$$F_{i,j} - UY_{i,j} \le 0, \quad \forall j \in \overline{H}, i \in P_j$$

$$F_j^w - UY_{w,j} \le 0, \quad \forall j \in \overline{H}$$

$$F_{j,out} - UY_{j,0} \le 0, \quad \forall j \in N$$

$$Y_{i,j}; Y_{w,j}; Y_{j,0} = 0,1$$

The Example 3 of MILP procedure is shown in Table 2.6. After applied the MILP, solution of minimum interconnection flowrates are generated shown in Table 2.7 and illustrated in Fig. 2.15.

Table 2.6 Limiting data for MILP Example 3 (Bagajewicz *et al.*, 2001)

Process	Mass load (kg/h)	$C_{in,max}$ (ppm)	$C_{out,max}$ (ppm)	Freshwater flowrate without reuse (t/h)
1	2	25	80	25
2	2.88	25	90	32
3	4	25	200	20
4	3	50	100	30
5	30	50	800	37.5
6	5	400	800	6.25
7	2	400	600	3.3333
8	1	0	100	10
9	20	50	300	66.6667
10	6.5	150	300	21.6667
	Total freshwater flowrate (ton/h)			**252.4167**

Table 2.7 Solution for MILP example 3 (Bagajewicz *et al.*, 2001)

Process	$F_{i,j}$ (ton/h)	Minimum Freshwater flowrate with reuse (ton/h)	Waste flowrate (ton/h)
1	0	25	0
2	0	32	0
3	$F_{1,3} = 7.14286$	15.7143	0
4	$F_{1,4} = 17.8571$	26.4286	0
5	$F_{4,5} = 20$	20	40
6	$F_{7,6} = 4.16667$ $F_{10,6} = 8.33333$	0	12.5
7	$F_{3,7} = 4.02857$ $F_{9,7} = 1.29524$	0	1.15714
8	0	10	0
9	$F_{2,9} = 32$ $F_{4,9} = 11.2$	36.8	78.7048
10	$F_{3,10} = 18.8286$ $F_{4,10} = 13.0857$ $F_{8,10} = 10$	0	33.571
Total flowrate (ton/h)		**165.9424**	**165.93294**

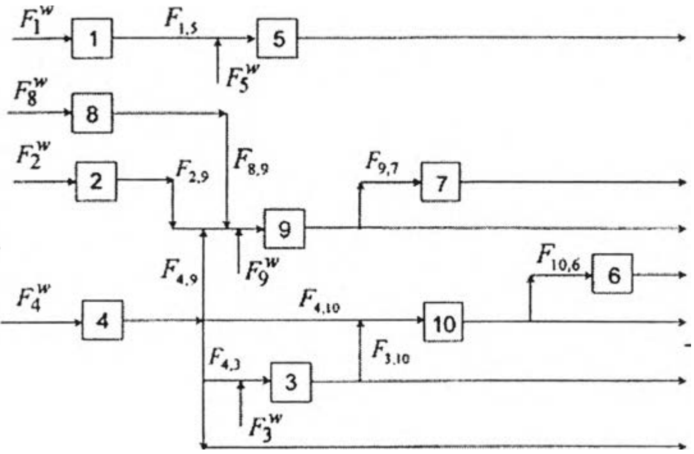

Figure 2.15 Minimum interconnection Water network (Bagajewicz *et al.*, 2001).

For fixed flowrate problem, mass integration design (Dunn *et al.*, 2001) is a technique for recycling many wastewater streams with multiple contaminants containing which called (Sources) to process water user (Sinks, Demands). They proposed a NLP model which based on general water allocation principles and uses the transshipment model to identify the water recycle network with multiple mapping diagram which shown in Fig. 2.16. Sources are mixing to satisfy sinks concentrations and flowrate. Wastewater is minimized simultaneously water recycle network is generated. The non-linear programming (MILP) mathematical model equations which are generated from the multiple mapping diagrams are shown below.

$$Min \sum_{i=1}^{Sources} Wastewater_i$$

Availability constraints for the sources

Overall mass balances: $$Source_i = \sum_{j=1}^{Sinks} Flow_{i,j} + Wastewater_i$$

Component balances: $$Source_i \cdot x_i^c = \sum_{j=1}^{Sinks} Flow_{i,j} \cdot x_i^c + Wastewater \cdot x_i^c$$

Availability constraints for sinks

Overall material balances: $$\sum_{i=1}^{Sources} Flow_{i,j} \leq FlowSink_j$$

Component constraint: $$\frac{\sum_{i=1}^{Sources} Flow_{i,j} \cdot x_i^c}{FlowSink_j} \leq y_j^c \max$$

Non-negativity constraints:

$Flow_{i,j} \geq 0$, i =1, 2, ...Sources, j = 1, 2, ... Sinks

Where $Source_i$ = Flowrate of source streams

$FlowSink_j$ = Flowrate of sink streams

$Flow_{i,j}$ = Flowrate from source to sink

x_i^c = Contaminant concentration of sources

$y_j^c \max$ = Maximum concentration of sinks

$Wastewater_i$ = Wastewater discharge of each source

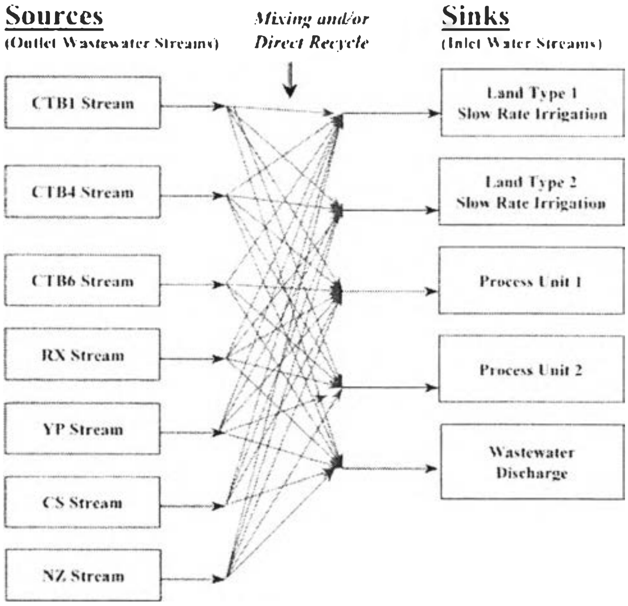

Figure 2.16 Multiple mapping diagrams (Dunn *et al.*, 2001).

Tan and co-workers (Tan *et al.*, 2007) do a retrofit water network of paper mill process by adding regeneration unit that target minimum freshwater and design by water cascade analysis and nearest neighbor algorithm. This exists process has six sinks and four sources, consumes 1989.06 ton/h of freshwater and discharges 1680.3 ton/h of wastewater. Pinch analysis was used to retrofit the water network of this process by design more complex network and add regeneration unit. Economics data of regeneration used to determine the most cost effective water network with regeneration units. Dissolve air floatation (DAF) which is physical treatment equipment that removes total suspended solids (TSS) from wastewater by bubble air is used for regenerate wastewater. The way to improve simple water network is add the DAF units for treat the wastewater and reuse it. The maximum regeneration flowrate ($F_{Reg,max}$) is sought by plot the freshwater flowrate versus regeneration flowrate as shown in Fig. 2.17. After do the water cascade analysis, they generate water network with treating unit that using 401.28 ton/h of freshwater and discharge 92.52 ton/h of waste with maximum regeneration flowrate by economics consideration.

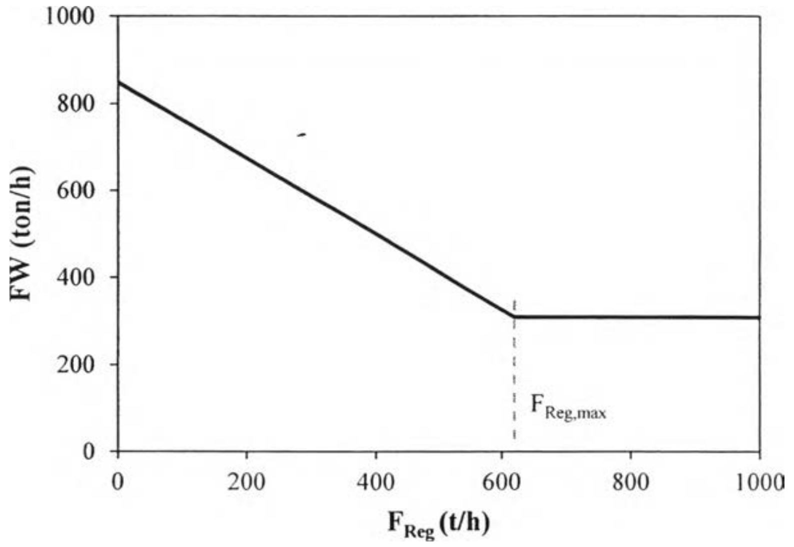

Figure 2.17 Freshwater flowrate versus regeneration flowrate.

Sotelo and co-workers (Sotelo-Pichardo *et al.*, 2011) proposed a new general mathematical programming model based on superstructure of water network with regeneration units as shown in Fig. 2.18, which is mixed-integer nonlinear programming (MINLP) for the optimal retrofit of mass conservation network considering recycle, reuse, and regeneration schemes. The model takes into account the reuse of existing treatment units and their modification as well as the introduction of new treatment units and the reconfiguration of the pipes to satisfy the stricter process and environmental constraints at minimum cost. The objective function includes the cost for the fresh sources, re-piping, and capital and operational costs for the treatment units in annual cost. They applied the general mathematical model to four specific cases. The solution is identified by MINLP model with appropriate initialization values of variables.

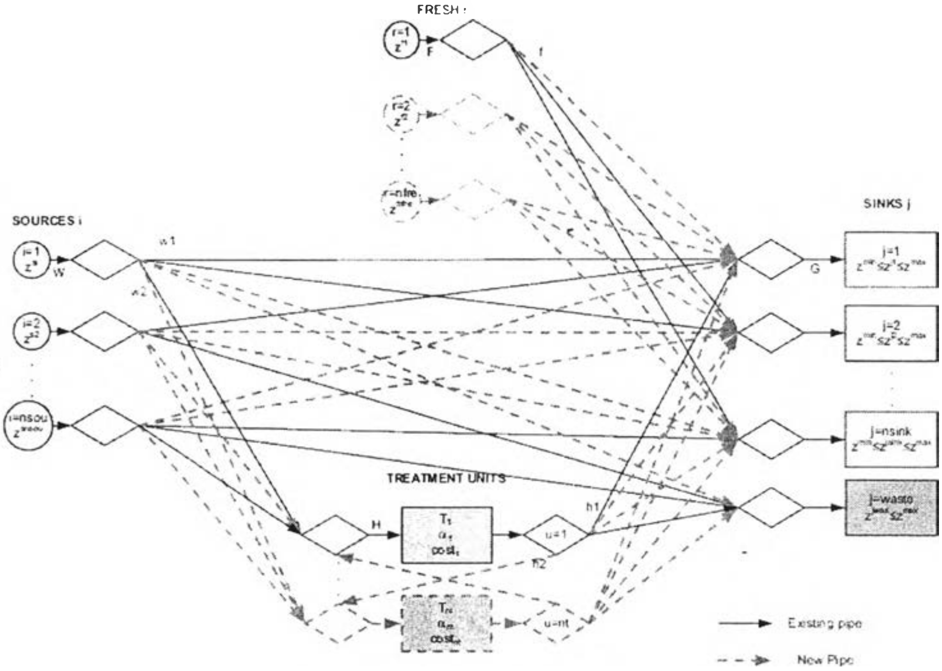

Figure 2.18 Superstructure of water network with regeneration units (Sotelo-Pichardo *et al.*, 2011).

2.4 Water network with heat integration

Over the last two decade, the synthesis and optimization of heat-integrated water networks have received considerable attention. The main objective was to simultaneously minimize water and energy. It was studied in order to provide process network using lowest amount of fresh water, cold utilities and hot utilities consumption. A lot of techniques were used to solve this problem but the most popular technique is mathematical programing

This topic was first addressed in 1998 by Savulescu and co-workers and be reviewed in recent year (Savulescu *et al.*, 2005a, Savulescu *et al.*, 2005b). They used a graphical method to solve the minimum of fresh water at the same time the minimum utility target illustrated by 4 operations that use water shown in Table 2.8. There are 4 operations at 4 different temperature (40, 100, 75 and 50 °C) and difference inlet/outlet concentrations. For instance, fresh water is fed at 0 ppm and 20 °C in addition; temperature of outlet stream is not over 30 °C. This pater is based on 2 stages approach.

Stage 1: They use the two-dimensional grid diagram shown in Fig 2.19. This grid represents a concentration scale on the horizontal axis and temperature scale on the vertical axis that each stream operations are positioning along the horizontal at limit inlet and outlet concentration and temperature. Not only available or require flow rates are known, but also concentration and temperature are identified. Then, the diagram was applied certain re-use rules. These rules suggest starting the reuse structure from the hottest source, connect processes near in temperature, and use non isothermal mixing.

Stage 2: minimum utility is identified by energy composite curve. Then, they apply a set of splitting rules to obtain vertical matching of the composite curve portions. A network of process to process and interconnection is in reality a sequential procedure that makes use of certain heuristics. However, these rules cannot guarantee that the resulting structure is optimal.

Table 2.8 Water-using operations data (Savulescu *et al.*, 2005a)

Operation	C_{in} (ppm)	C_{out} (ppm)	$T_{op,in}$ (°C)	$T_{op,out}$ (°C)	Water flowrate without reuse (kg/s)	Mass load (g/s)
1	0	100	40	40	20	2
2	50	100	100	100	100	5
3	50	800	75	75	40	30
4	400	800	50	50	10	4

Temperature of freshwater source Tin = 20 °C

Temperature of discharge waste Tin = 30 °C

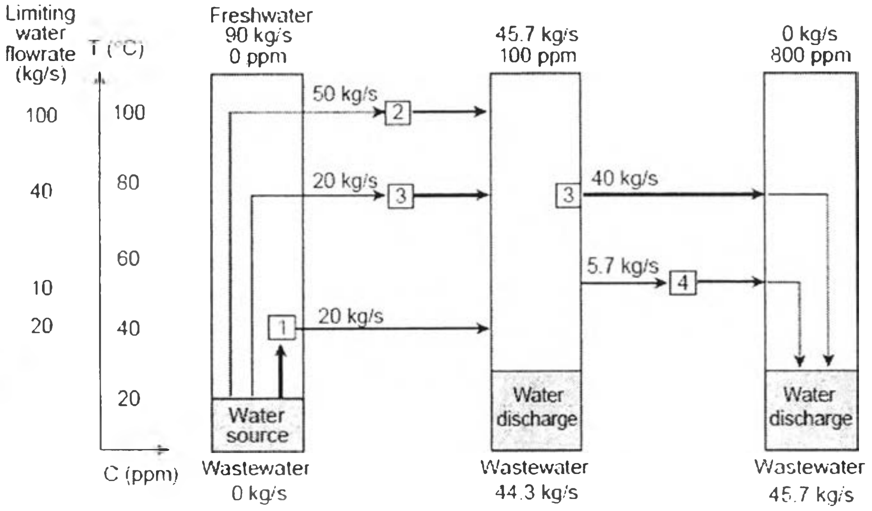

Figure 2.19 Two-dimensional grid diagram (Savulescu *et al.*, 2005b).

For the last ten years, Bagajewicz and co-worker (Bagajewicz *et al.*, 2002) proposed an MILP mathematical model for minimum utility targeting. To build model, they consider the use of a Pinch operator and a simplified version of the state-space (Bagajewicz *et al.*, 1998). Fig. 2.20 shows a state-space representation of the problem. A freshwater stream enters the distribution network where it is split and sent to several junctions. These junctions also collect wastewater from processes (represented by pollutant operator) and from heat exchanger (represented by a pinch operator).

In turn, the pollutant operator has for this case the form of a superstructure operator (Bagajewicz *et al.*, 1998), that is, each junction is connected to only one process. This is schematically shown in Fig. 2.21. Process streams transfer pollutants to the water.

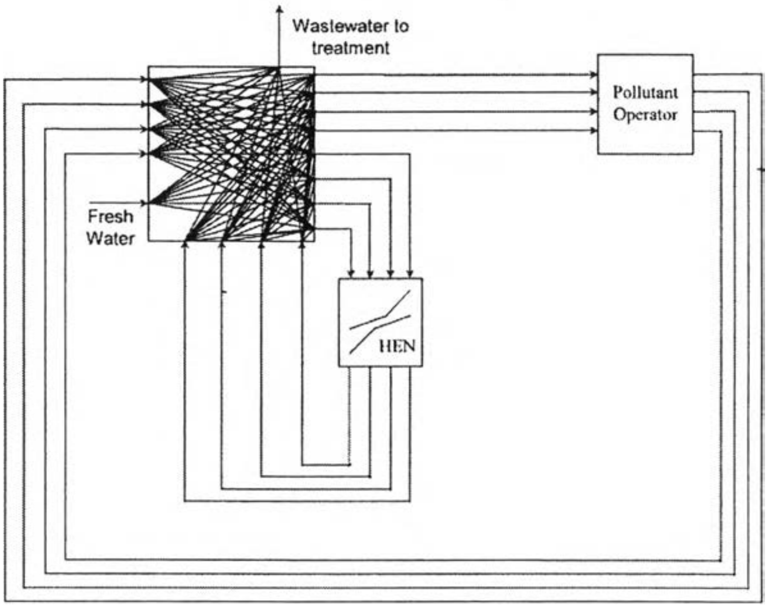

Figure 2.20 State-space approach representation (Bagajewicz *et al.*, 2002).

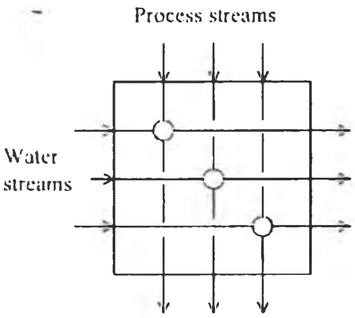

Figure 2.21 Superstructure operator (Bagajewicz *et al.*, 1998)..

Bogataj and Bagajewicz (Bogataj *et al.*, 2008) proposed an approach for the simultaneous synthesis of energy efficient water network using mathematical programming and superstructure optimization. They modified the HEN which call "stage-wise superstructure" (Yee *et al.*, 1990) for the mixing and splitting streams within HEN superstructure which shown in Fig. 2.22. Isothermal mixing and non-isothermal mixing are both occurred in this model. Heat is transfer by non-isothermal mixing (direct exchange) and heat exchanger (indirect exchange) (Savulescu *et al.*, 2002). They combine this model with water network. The combined model was solved by a two-step solution method. First step; water network are solved by non-linear programming model which have objective function to minimize the water related cost. Step two; they solve the combined water network and HEN which is MINLP model to obtain the continuous variables (flowrate, temperature, etc.).

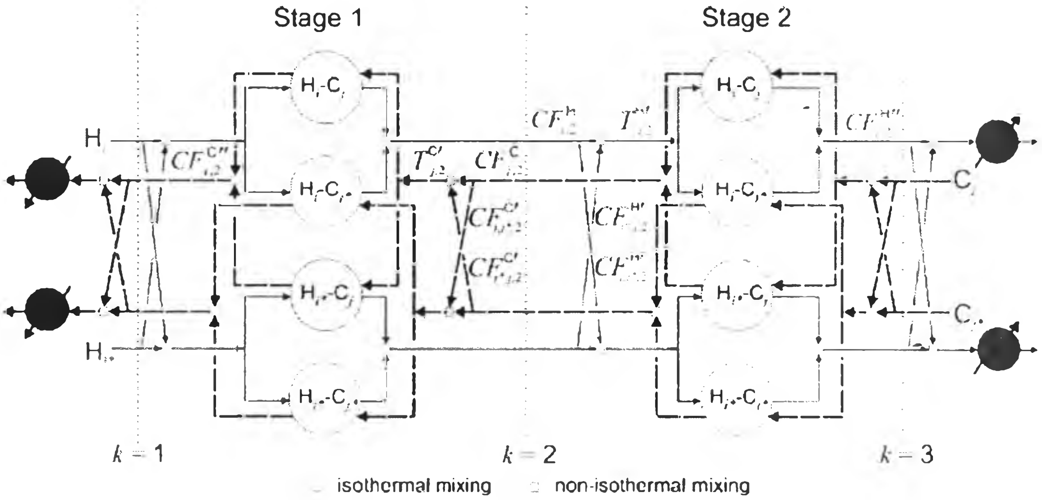

Figure 2.22 Modified HEN superstructure (Bogataj *et al.*, 2008).

Dong and co-workers (Dong *et al.*, 2008) modified the state-space super structure (Bagajewicz *et al.*, 1998) for simultaneously synthesizing water network and HEN. In this model, all possible water reuse are considered. Distribution network make all stream possibly re-use, and direct and indirect heat exchange opportunities as well.

The problem was formulated as an MINLP. The feasible solutions were produced using randomly-generated initial estimations followed by improving the candidate solutions using perturbation techniques, and generating alternative network structure by shifting heat loads in loops along the utility paths. This approach can be used for single and multiple contaminant problems. In addition, they proposed the utility cost, fresh water cost and investment cost parameters which be used in recent works for water network comparison which shown in Table 2.9.

Table 2.9 Cost and operating parameters (Dong *et al.*, 2008)

Parameter	
Freshwater cost	0.375 $\$/\mathrm{t}$
Cooling utility (cooling water) cost	189 $\$/(\mathrm{kW\ a})$
Heating utility (low pressure steam, 120 °C) cost	377 $\$/(\mathrm{kW\ a})$
Fixed charge for heat exchangers	8000 $\$$
Area cost coefficient for heat exchangers	1200 $\$/\mathrm{m}^2$
Cost exponent for exchangers	0.6
Overall heat-transfer coefficient (individual heat-transfer coefficients for streams and utilities were assumed to be 1 kW(m^2 °C)	0.5 kW/(m^2 °C)
Working hours of plant per year	8000 h
Temperature of freshwater	20 °C
Temperature of wastewater	30 °C
The inlet and outlet temperature of cooling water	10 °C and 20 °C
Specific heat capacity of water	4.2 kJ/(kg °C)

Leewongtanawit and Kim (Leewongtanawit *et al.*, 2009) presented a graphical approach for the design of heat-integrated water networks. This approach was based on Water and Energy Balance Diagram which is an extension of the two-dimension grid diagram (Savulescu *et al.*, 1998). The design interactions between water network and HEN were explored and energy-efficient and cost-effective configurations for heat recovery were identified.

Liao and co-workers (Liao *et al.*, 2011) introduced a step-wise systematic procedure (Yee *et al.*, 1990) for the system of heat-integrated water network, and proposed procedure for the identification of the promising matches between hot and cold streams within water network, followed by targeting and design steps. For targeting step, the identification of the promising matches between hot and cold streams was performed, whilst in the design step, a stage-wise superstructure was used to deal with the features of mixing and splitting inside HEN. The problem was formulated as a MINLP, only single contaminant problem was considered.

Polley and co-workers (Polley *et al.*, 2010) developed a simple methodology based on a design insight for the designing of water network and HEN. They demonstrated that water network and HEN can be separately solved. The resulting network exhibited the minimum water and energy consumption, and provides simple structure for single component problem.

Patino and co-workers (Martínez-Patiño *et al.*, 2012) proposed a heuristic procedure for simultaneous synthesis of water and energy networks. They start by looking at the interactions between water, energy and network structure. This analysis provides the required background and guidelines for developing a new methodology for the synthesis of networks. They used s temperature vs. concentration diagram to guide the design of an initial configuration of the heat and mass exchange network. Some improvements are implemented in order to minimize the energy requirements.

In addition, they found that the network with non-isothermal mixing have less heat exchanger than isothermal mixing.

Siemanond and co-worker (Siemanond *et al.*, 2012) proposed a retrofit HEN of crude distillation unit (CDU) using stage model (Tjoe *et al.*, 1986) to reduce hot and cold utilities consumption. A simple pinch design approach is proposed to accomplish above-and-below-pinch HEN design, which is efficient procedure to do retrofit HEN with optimal result.

Ahmetovic and co-workers (Ahmetović *et al.*, 2013) presented a superstructure of combined water and heat exchanger network. They also use direct and indirect heat exchange theory to generate minimum number of heat exchangers. They use the data from (Savulescu *et al.*, 2005a) (Table 8) where objective is to minimize the total annual cost. The model is non-convex MINLP shown in Fig. 2.23. The model have many possibility of mixing-and splitting, freshwater is heated by utilities before intake to process and outlet stream from process have a chance to combine inlet stream. There developed network use lowest heat exchanger area and lowest total annual cost compare with other model from previous literature.

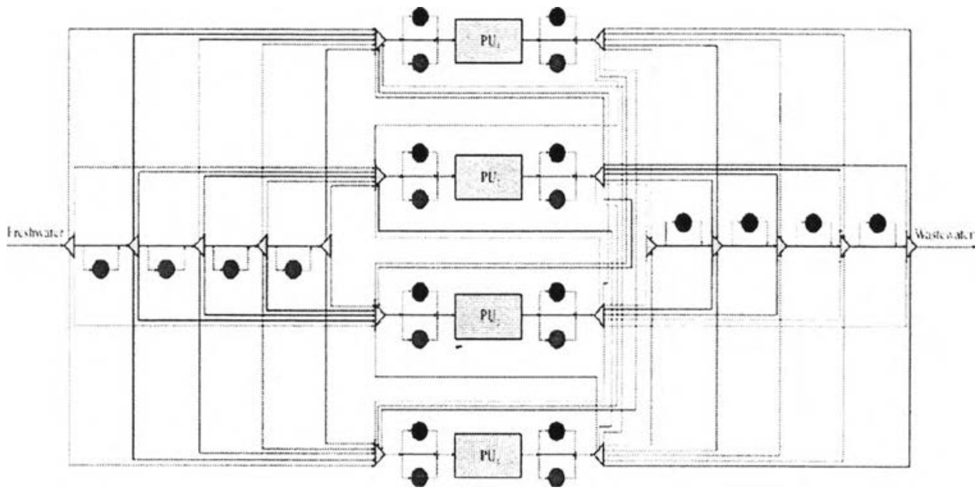

Figure 2.23 Combined water and heat superstructure (Ahmetović *et al.*, 2013).