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# Wastewater Minimization in a Chlor-Alkali Complex

Zuwei Liao, Jingdai Wang and Yongrong Yang Department of Chemical and Biological Engineering, Zhejiang University P. R. China

#### 1. Introduction

Water network integration is one of the most efficient technologies for wastewater reduction <sup>[1]</sup>. During the past two decades, both the water pinch technology and the mathematical programming method have been frequently discussed and widely applied in the industry. The water pinch technology divides the water network integration into two steps: targeting and design. This technology was initiated by Wang and Smith <sup>[2]</sup> in 1994. They treat the water using operation as a mass transfer unit and use concentration vs mass load coordinate to obtain the minimum freshwater consumption of the whole system. Based on this coordinate system, the targets of wastewater reuse and regeneration reuse are established. The methods of Wang and Smith <sup>[2, 3]</sup> have been well supplemented by many authors in recent years.

The first supplement is on the model of the water using operation. It is obvious that not all the water using operations are the mass transfer type. Typical water using units like cooling tower, boiler and reactor are not this kind. Actually, these units are flow rate fixed operations. To treat operations in this category, targeting methods in different coordinates were developed. Dhole et al.<sup>[5]</sup> obtained the composite curve in concentration vs flow rate coordinate, which has been supplemented by several works <sup>[6-9]</sup>. Hallale <sup>[6]</sup> introduced a water surplus diagram and obtained the real target. El-Halwagi et al. <sup>[8]</sup> and Prakash and Shenoy<sup>[9]</sup> developed a mass load vs flow rate composite by analogy to the heat integration system. In addition, Agrawal and Shenoy<sup>[10]</sup> achieved the freshwater target in the concentration vs mass load coordinate; Bandyopadhyay et al.<sup>[11, 12]</sup> calculated the wastewater target in the same coordinate. Recently, Pillai and Bandyopadhyay <sup>[13]</sup> established a simple and more effective algebraic methods for fixed flow rate operations, and they can be extended to cases of multiple water sources <sup>[14-16]</sup>. The targeting concept is also applicable to process changes <sup>[11, 17]</sup> and threshold problems <sup>[18]</sup>.

The second supplement is on the regeneration target. The regeneration has two cases: regeneration reuse and regeneration recycle. For regeneration reuse, Wang and Smith <sup>[2]</sup> proposed that the regeneration concentration should be at the pinch concentration. Latter, Mann and Liu <sup>[19]</sup> pointed that the optimum regeneration concentration can be above the pinch. Feng et al. <sup>[20]</sup> introduced a targeting method for regeneration recycle, which has been extended to the regeneration reuse system <sup>[21]</sup> and the zero discharge system <sup>[22]</sup>. On the other hand, the regeneration problem for fixed flow rate problems are more complicated than the fixed mass load problems, because the regeneration flow rate is constrained by

water sources. Agrawal and Shenoy <sup>[10]</sup> adopted the method of Wang and Smith <sup>[2]</sup> to treat this problem. Bandyopadhyay et al. <sup>[23]</sup> considered the regeneration recycle problem. Ng and Foo et al. <sup>[24, 25]</sup> divided the system into two blocks: the regeneration block and the freshwater block where the final targets are obtained.

The third supplement is on the wastewater treatment minimization. After the freshwater and regeneration water targets are determined, Kuo and Smith <sup>[26, 27]</sup> addressed the wastewater treatment problem by constructing the wastewater composite curve. Bandyopadhyay et al. <sup>[12]</sup> established the wastewater and wastewater treatment targets simultaneously in their source composite curve. Ng and Foo <sup>[28, 29]</sup> obtained the target by determining the wastewater flows.

The earliest design method for the water network is the "grid diagram" proposed by Wang and Smith <sup>[2]</sup>. To avoid the tedious steps of the method, Olesen and Polley <sup>[30, 31]</sup> developed the load table method. Subsequently, design rules based on "water main" <sup>[27, 32]</sup>, "internal water main" <sup>[33]</sup> and other heuristic rules <sup>[34]</sup> are introduced. All these methods are focused on fixed mass load problems.

According to the necessary condition proved by Savelski and Bagajewicz <sup>[35]</sup>, the methods for fixed flow rate problems are also suitable for fixed mass load problems. El-Halwagi <sup>[36]</sup> first designed the fixed flow rate problem by "source-sink" method. Prakash and Shenoy <sup>[9]</sup> introduced the nearest neighborhood algorithm, and proved its optimality. Later, they <sup>[37]</sup> reduced the number of connections by matrix operating. Ng and Foo <sup>[38]</sup> got the same target via a "water using path". Bandyopadhyay <sup>[13]</sup> proved that there is no cross pinch matches between water sources and demands under the optimal condition. Recently, Alwi and Manan<sup>[39]</sup> distributed the sources in the light of the source-sink composite curve. Moreover, total annual cost based design <sup>[40]</sup>, retrofit design <sup>[41-43]</sup> and optimizing software <sup>[44]</sup> are becoming the next hot topic of this area.

The well developed water network integration technology has been widely applied in the industry. The most successful application should be in the refinery and petrochemical industry <sup>[45-47]</sup>. In 1980, Takama <sup>[48]</sup> reported the first refinery application which reduced 24% of the freshwater consumption. Wang and Smith <sup>[2]</sup> proposed 47.6% of further reduction by regeneration reuse. In 1997, Liu <sup>[19]</sup> increased the water reuse percentage from 18.6% to 37% in some petrochemical complex of Taiwan. In addition, the water integration technology has also been applied to the pulp and paper plant <sup>[41, 49, 50]</sup>, sugar plant <sup>[51]</sup>, pesticide <sup>[52]</sup>, textile <sup>[53]</sup> electroplate <sup>[49, 54]</sup> clean agent <sup>[55]</sup> fuel <sup>[56]</sup>, catalyst <sup>[57]</sup> and steel industry <sup>[58]</sup>.

We will use the well developed water pinch technology to the chlor-alkali industry. The chlor-alkali industry consumes huge amount of freshwater. Some large chlor-alkali complex takes dozens of million tons of freshwater every year. In certain area, the chlor-alkali industry occupies 1/4 to 1/3 of the total water consumption of the area, which causes the shortage of the freshwater supply. On the other hand, the chlor-alkali industry also discharge large amount of wastewater, while the environmental regulation is getting stricter. Therefore, it is very urgent for the chlor-alkali industry to improve their water using efficiency and carry out wastewater minimization.

#### 2. The chlor-alkali complex and its water system

#### 2.1 Complex description

The chlor-alkali complex processes brine and produces 40 kt caustic soda, 10 kt chlorine liquid, 20 kt hydrochloride, 8000 t bleaching powder every year. The complex includes 5

plants in which there are many subsections. The schematic flow sheet of the complex is shown in figure 1. Plant 1 is composed of one salt dissolving section, two evaporation sections, one solid caustic soda section and a boiler section. Plant 2 mainly includes chlorine drying section and the sections of various chlorine by products. The chlorine by products are chlorine liquid, hydrochloride, perchloravinyl, chlorinated paraffin, sodium hypochlorite. Plant 3 is the electrostenolysis plant which involves three set of electrostenolysis equipments. The hydrogen and chlorine products from this plant are sent to plant 1 and plant 2 respectively. Plant 4 is the bleaching powder plant while plant 5 is the utility plant. The utility plant has seven set of circulating cooling water systems and one set of pure water producting system. With all these processes and products, the whole system consumes huge amount of water as shown in table 1. In order to find the full range of water saving space, the water balance of the existing system should be addressed first, and this is implemented in the next section.

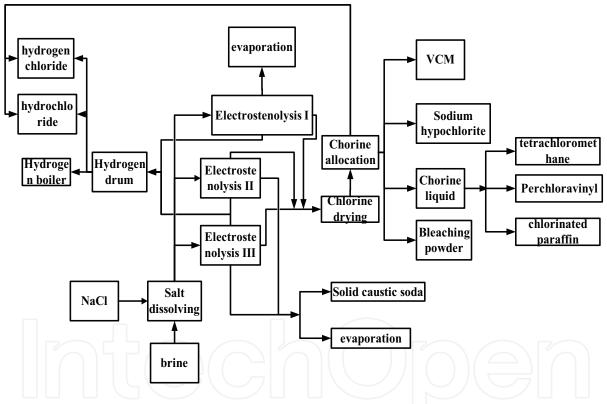


Fig. 1. Schematic flow sheet of the chlor-alkali complex

Plants	Water comsumption(t/d)		
1	9683		
2	25176		
3	21303		
5	1076		

Table 1. Freshwater consumption of the chlor-alkali complex

#### 2.2 The balanced water system of the complex

#### 2.2.1 Plant 1

The balanced water system of plant 1 is shown in figure 2. Now, let's analysis the plant section by section.

#### Salt dissolving section

This section consumes freshwater  $(39m^3/h)$ , steam condensate  $(68.5m^3/h)$  and resin washing water  $(15m^3/h)$ . These water sources are used to prepare refining agent, flocculants, to wash brine sludge, to cool pump. While all the discharged water is sent to dissolve the salt. The main constraint contaminant is the organic content which is represented by COD.

#### **Electrostenolysis section**

Water is used for hydrogen washing in this section. The washing unit consumes 50m<sup>3</sup>/h freshwater. The effluent from the washing unit is COD free, but contains trace amount of caustic soda. Therefore, it suggested to be used in the cooling water system.

#### **Evaporation section**

The evaporation section involves triple-effect distillation and double-effect distillation whose products are 30% and 48% alkali liquid respectively. The triple-effect distillation yields 80 m<sup>3</sup>/h steam condensate. Some condensate is sent to the cooling water system, which cause additional cooling load. Others are used in dissolving salt and washing the evaporator. Moreover, this section needs 10 m<sup>3</sup>/h pump cooling water. The double-effect distillation produces 25 m<sup>3</sup>/h steam condensate. 16 m<sup>3</sup>/h of the condensate is utilized as boiler feed water, while 9 m<sup>3</sup>/h of the condensate is sent to salt dissolving. In summary, the evaporation section produces 105 m<sup>3</sup>/h condensates. The condensates are used in salt dissolving, boiler feed, washing and cooling system. The reuse in dissolving and boiler feed recovers both the energy and water quality well. But the condensate used in cooling system is on the contrary. Therefore, they should be reused in other units.

#### Solid caustic soda

This section discharges  $6 \text{ m}^3/\text{h}$  steam condensate.

#### 2.2.2 Plant 2

#### Hydrochloride and high purity hydrochloride section

The HCl is absorbed by freshwater and the discharge water from the chlorinated paraffin section. The hydrochloride process welcomes water of weak acid. Also note that COD is the control contaminant. Thus, some acid wastewater might be reused here. On the other hand, the high purity hydrochloride process only consumes pure water.

#### Perchloroethylene section

This section consumes  $140m^3/h$  freshwater and discharges  $135m^3/h$  wastewater, where wastewater of  $133 m^3/h$  is cooling water discharge. This cooling water should be recycled in the cooling water system or reused in other units. The remaining freshwater are used in dissolving solid caustic soda ( $5m^3/h$ ) and washing ( $2m^3/h$ ).

#### Chlorinated paraffin section

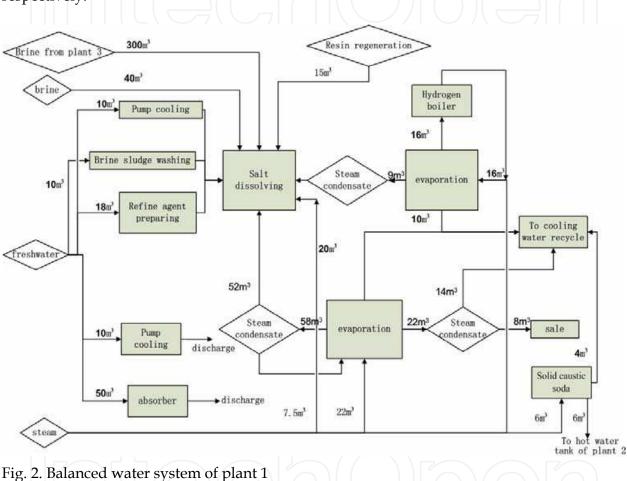
The chlorinated paraffin section discharges

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In this section, the flow rate of cooling water discharge is 48 m<sup>3</sup>/h. This discharge should be recycled. The freshwater is also used in tail gas absorption, and the discharge water has been reused in the hydrochloride process.

#### White carbon black section

The freshwater consumption of the white carbon black section is 27m<sup>3</sup>/h. The freshwater is mainly used in absorbing and cooling. Air absorber cooling consumes 5m<sup>3</sup>/h, while the consumption of tail gas absorber, acid gas absorber and discharge absorber are 6, 6, 10 m<sup>3</sup>/h respectively.



### Sodium hypochlorite section

This section has two streams of cooling water that are not recycled. They are the cooling water of the absorber and cooler whose flow rates are 16m<sup>3</sup>/h and 43m<sup>3</sup>/h respectively.

#### Chlorine drying section

The freshwater consumption is totally direct discharge cooling water. The discharged cooling water includes the tail gas column cooling, chlorine water cooling and the chlorine cooling.

#### **Chlorine liquid section**

Despite of direct discharging water, the freshwater are also used for bottle washing and hot water tank supplement.

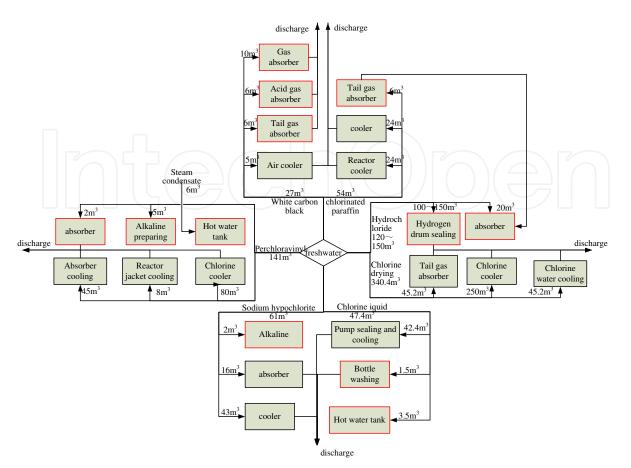


Fig. 3. Balanced water system of plant 2

#### 2.2.3 Plant 3

Plant 3 only consumes pure water, and the pure water flow rate is 55 m<sup>3</sup>/h. The pure water is used in the electrolyzer feed and pump sealing. The discharge of pump sealing water could be reused in the resin regeneration. In addition, the batch process of filter washing and resin regeneration consume 360 m<sup>3</sup> pure water per day, while the discharge is sent to dissolving salt.

#### 2.2.4 Plant 5 utility plant

This plant is composed of the pure water production process and the cooling towers. The capacity of the cooling towers is 9000 m<sup>3</sup>/h, and the makeup freshwater is 145 m<sup>3</sup>/h and the discharge water is 72 m<sup>3</sup>/h. The pure water is produced from the freshwater, and the production rate is 80 m<sup>3</sup>/h. The cooling towers are divided into six separate systems. Current, only the cooling system for chlorine liquid has some spare capacity.

#### 3. Evaluate and design of the water system

The whole water system of the complex is composed of the process water allocation system and the cooling water system. The interactions of these two systems are presented in figure 5. The freshwater are supplied to the process units. After mass transfer and reaction processes, wastewater is discharged. Since the quality of the cooling water is not degenerated during the heat transfer process, most of them can be recycled. The recycling of the cooling water is mainly constrained by the capacity of the cooling tower. Therefore, we design the system in two steps: first determine the cooling water network, second the un-recycled cooling water are involved in the next design step of process water allocation system.

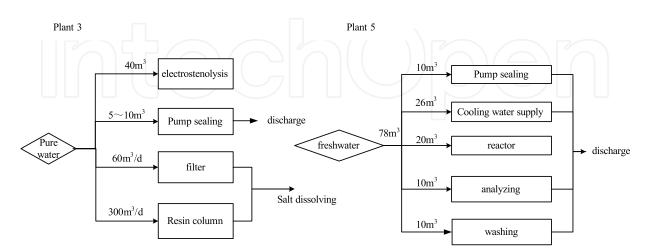
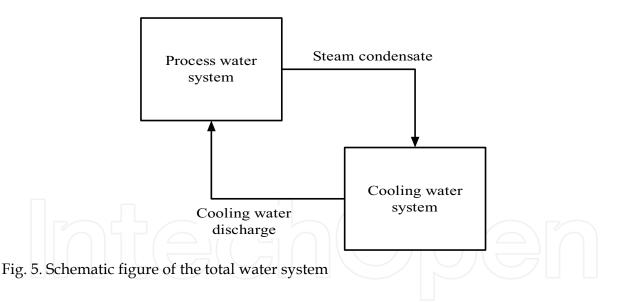


Fig. 4. Balanced water system of plant 3 and 5



#### 3.1 Retrofit of cooling water system

At present, 6 out of 8 cooling water recycle is overburdened at summer season, while the other 2 are not at their maximum capacity. Meanwhile, the cooling load should be enlarged because several direct discharge cooling water will be recycled. Moreover, additional cooling load of 450t/h is required for a new process. Consequently, the capacity of the current cooling system should be checked.

Table 2 illustrates the direct discharge cooling water that can be recycled. The cooling loads are mainly distributed in plant 2. From Table 2, only the items in bold are allowed using circulating cooling water, because process safety and other practical constraints.

Plant/process	Unit
Plant 1 Electrostenolysis section	Hydrogen washing
Plant 2 chlorine drying section	Chlorine cooler
Plant 2 chlorine drying section	Tail gas cooler
Plant 2 chlorine drying section	Chlorine water cooler
Plant 2 Perchloroethylene section	Perchloroethylene cooler
Plant 2 Sodium hypochlorite section	cooler
Plant 2 new chlorinated paraffin section	cooler

Table 2. List of direct discharge cooling water

Heat load(kkcal/h)	1450.18	126.983
Cooling water flow rate(t/h)	45.2	250
Cooling water initial temperature (°C)	28	28
Cooling water end temperature (°C)	60.08	28.51

Table 3. Parameters for the cooling of the chlorine drying process

Table 4 presents the parameters of the cooling water in the perchloravinyl section, the new chlorinated paraffin section and the chlorine water section. Table 5 and 6 show the current conditions for the cooling water system and the cooling tower of the chlorine liquid system. Since the cooling range of the cooling tower lies between 32°C and 42°C, the difference of these cooling streams should be adjusted. Table 7 illustrates the adjusted condition where the heat load is unchanged.

process	Perchloroethylene	Chlorine water cooling	Chlorinated paraffin
Inlet temperature (°C)	28	28	32
Outlet temperature (°C)	53	60	37
Heat load (KW)	3208.3	1687.5	2625
flow rate (m <sup>3</sup> /h)	110	45.2	450

Table 4. Cooling water temperature and its heat load

	York units	Water chilling units
Inlet temperature (°C)	32	32
Outlet temperature (°C)	42	34
flow rate $(m^3/h)$	1072.5	450

Table 5. Condition of the circulating cooling water for the chlorine liquid process

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item	value	Air volume flow rate(m <sup>3</sup> /h)	505000
		Air mass flow rate(kg/m <sup>2</sup> s)	3.07
Thermal property function	N=1.747×(λ0.4675)	Water flow rate(kg/h)	2.1×106
Filling type	Double taper thin film	water-spraying density (m <sup>3</sup> /m <sup>2</sup> h)	13.5
Filling shape	TX- II	Vapour/water ratio	0.82
Filling height (m)	1.5	Inlet temperature(°C)	42
Cross sectional area (m <sup>2</sup> )	51.84	Outlet temperature(°C)	32
wet-bulb temperature (°C)	28	Temperature difference(°C)	10

Table 6. Parameter for the cooling tower for chlorine liquid section

	Perchloroethylene	Chlorine water cooling	Chlorinated paraffin
Inlet temperature (°C)	32	32	32
Outlet temperature (°C)	42	42	37
flow rate $(m^3/h)$	275	145	450

Table 7. Circulating cooling water conditions

If the cooling units are arranged in parallel mode as shown in figure 6, then the cooling outlet parameters are illustrated in table 8.

	at present	after retrofit
Outlet temperature	39.64°C	39.50°C
flow rate of circulating water	1522.5 m³/h	2392.5 m³/h
heat load of circulating water	13562kw	21087kw

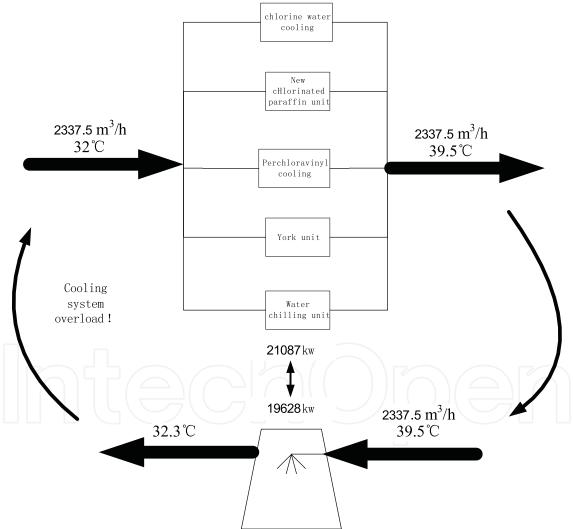
Table 8. The cooling water outlet parameter under parallel condition

Combining the outlet condition in table 8 with the cooling tower parameters in table 6, one can obtain the performance of the cooling tower by running the cooling tower model<sup>[59]</sup>. The calculated result is shown in figure 6. From the figure, we can see that the outlet temperature of the cooling tower is higher than the required process cooling water inlet temperature. The heat load of cooling water system (21087KW) is larger than that of the cooling tower. Therefore, the cooling tower is overburdened. There is a bottleneck inside the system.

To eliminate the bottleneck, both the cooling tower and cooling water network should be modified. First, the cooling water inlet and outlet temperature of each process units are increased to their maximum value. This is because increasing the water inlet temperature will improve the heat load of the cooling tower. The limiting temperatures are presented in table 9.

	Perchloroethylene	Chlorine water cooling	Chlorinated paraffin
Inlet temperature (°C)	37	37	32
Outlet temperature (°C)	52	50	37
flow rate (m <sup>3</sup> /h)	183.3	111.5	450
	York units	Water chill	ing units
Inlet temperature (°C)	32	32	
Outlet temperature (°C)	42	34	
flow rate $(m^3/h)$	1072.5	450	0

Table 9. Cooling water operating parameter under limiting temperature condition



Cooling tower for chlorine liquid cooling water

Fig. 6. The relationship between the cooling water network and cooling tower under the parallel condition

If the cooling water from one unit could be reused in another unit, then the total flow rate will be further decreased. The minimum cooling water flow rate can be determined by pinch analysis <sup>[59]</sup>. The "temperature vs enthalpy" diagram of the system is shown in figure 7. This composite curve is similar to the "contaminant vs mass load" diagram in water allocation networks, and the minimum cooling water flow rate is obtained as 1972.5m<sup>3</sup>/h.

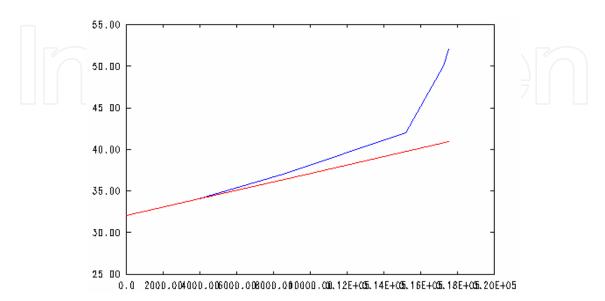


Fig. 7. Cooling water composite curve

To achieve the minimum cooling water consumption, sequential structures should be introduced to the cooling water network. On the other hand, the maximum cooling water flow rate is achieved by completely parallel structure. Both the maximum and minimum cooling water supply lines are presented in figure 8. Consequently, the region between these two lines is the feasible supply region, which is shown in shadow.

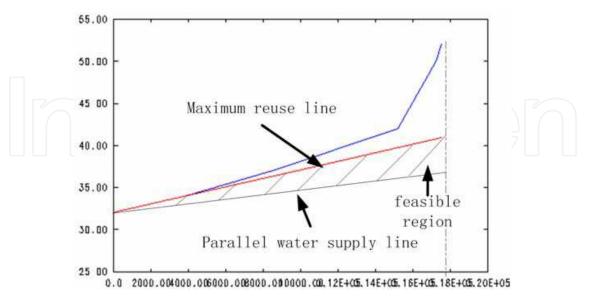
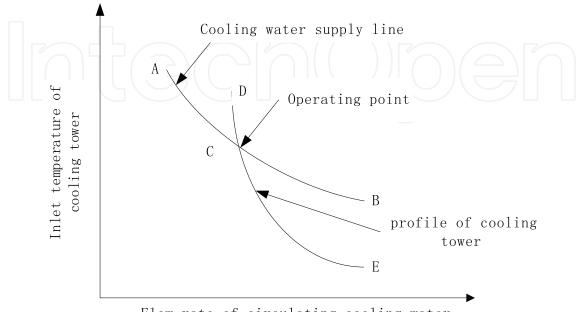


Fig. 8. The range of cooling water supply

It should be noted that all the supply lines inside the feasible region have the same heat load: 21087 kw. But the outlet temperatures and flow rate are different. This will lead to the

change of cooling tower heat load. In addition, the design of cooling water network must satisfy the following requirements: (1) the heat load of cooling water network matches the heat load of cooling tower; (2) the inlet temperature of cooling water network cannot exceed 32°C.



Flow rate of circulating cooling water

Fig. 9. Cooling tower profile and the cooling water supply line

To achieve the first requirement, we should find an operating point that satisfies both the network and the cooling tower. The operating point will be obtained via figure 9. In the figure, the vertical and horizontal axes are cooling tower inlet temperature and flow rate respectively. Under the same heat load, we can draw a cooling water supply line and a cooling tower working profile in this coordinate system. As shown in figure 9, the curve ACB is the cooling water supply line which represents the relationship between the outlet temperature of the cooling tower, which is obtained by cooling tower simulation under the fixed air flow rate (505000m<sup>3</sup>/h) and outlet temperature (32°C). At the intersection point C of the curve ACB and DCE, the outlet temperature of the cooling water network equals the inlet temperature of the cooling tower. Moreover, the flow rate and heat load of the two systems are also identical. Therefore, point C satisfies all the requirements, it is the operating point. In this case, the cross sectional point C is at temperature 41.146°C and flow rate 1972.5 m<sup>3</sup>/h which is the minimum cooling water flow rate.

The next step is to design the cooling water network under the determined temperature and flow rate. The network design procedure is similar to that of the process water network, and is not repeated here. Applying the design method, two final network structures are obtained as shown in figure 10 and 11.

The first solution shown in figure 10 includes the following reuse scheme: the outlet flow of water chilling units is sent to the chlorine water cooling and perchloroethylene cooling units. As shown in figure 11, the reuse source is shifted to the cooling water from new chlorinated paraffin unit in solution 2.

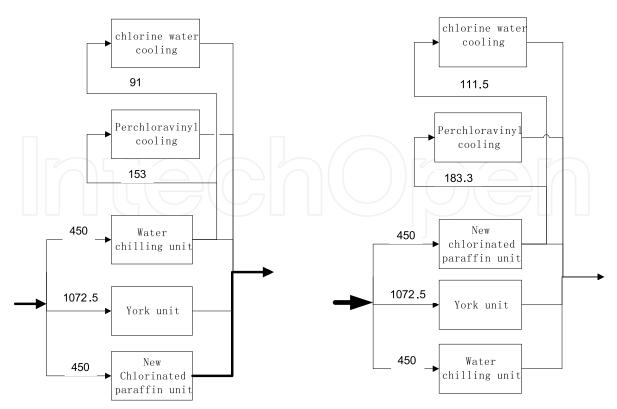


Fig. 10. Cooling water system retrofit solution 1

Fig. 11. Cooling water system retrofit solution 2

#### 3.2 Optimization of the process water allocation system

After determining the cooling water network system, it is term for optimizing the process water allocation network. The optimal design will be carried out via both pinch technology and mathematical methods. As this is a practical case, the procedure includes four steps: evaluate the existing system, determine water sources and sinks and the required flow rate, complement the limiting water using data, and finally the network design.

Step 1. evaluate the existing water system

The direct reuse choices within single units are considered in this step. Based on the introduction in the previous section, three choices are selected in this step:

In white carbon black section, the gas cooling water can be used to absorb the tail gas. This direct reuse of cooling water avoids the pumping cost of cooling water recycle system. 5 m3/h of freshwater can be saved, and it is no additional cost.

In the utility plant, the pump seal water can be reused as the supplement water for the cooling tower.

In the utility plant, the resin regeneration water can be reused for reverse washing.

Step 2. determine water sources and sinks and the required flow rate

The water using operations of the whole chlor-alkali complex are listed in table 10.

**Step 3.** complement limiting process data

In this step the contaminants and their limiting concentration will be provided via analysis, comparison and assumption.

For the whole complex, most of the processes are inorganic chemicals except the perchloravinyl and chlorinated paraffin section in plant 2. Normally, the wastewater from these inorganic sections does not have organic composition. Therefore, organic

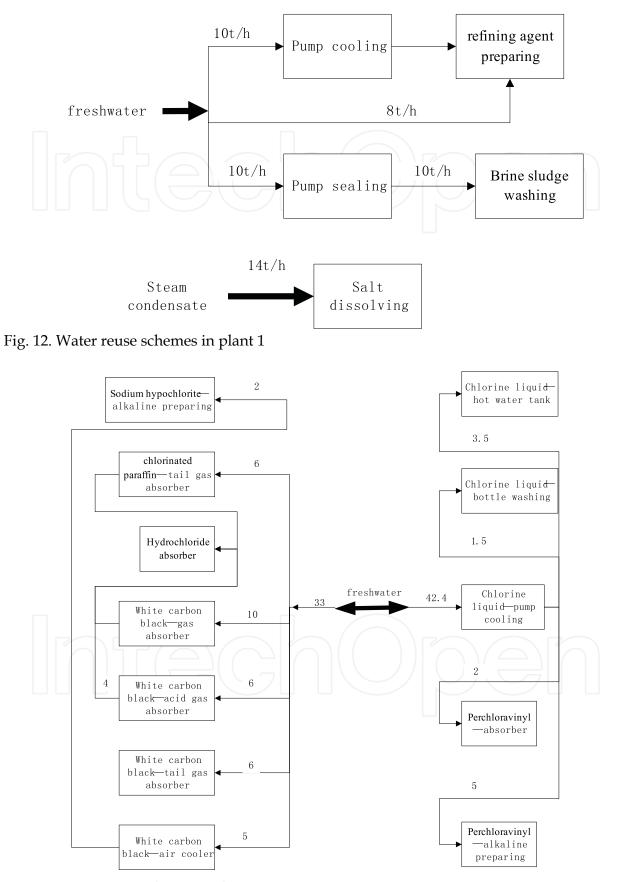
Process	unit	limiting flow rate (m <sup>3</sup> /h)	Current source
Perchloravinyl	Alkali solution preparation	5	freshwater
	Hot water tank	6	freshwater
	Absorber	2	freshwater
Sodium hypochlorite	Alkali solution preparation	2	freshwater
Chlorine liquid	Bottle washing	1.5	freshwater
	Hot water tank	3.5	freshwater
hydrochloride	absorber	20	freshwater
chlorinated paraffin	Tail gas absorption	6	freshwater
White carbon black	absorber	10	freshwater
	Acid gas absorption	6	freshwater
	Tail gas absorption	6	freshwater
	Gas cooling	5	freshwater
electrostenolysis	Electrostenolysis tank	40	Pure water
	Resin regeneration	15	Pure water
	Pump sealing	7.5	Pure water
Bleaching powder	Pump sealing	10	freshwater
	Recycle supplement	20	freshwater
Utility	Cooling tower supply	26	freshwater
	washing	10	freshwater
Salt dissolving	brine sludge washing	10	freshwater
	Salt dissolving	15	Resin regeneration
	Pump cooling	10	freshwater
	Refining agent preparing	18	freshwater
Solid caustic soda	Steam condensate	6	
evaporation	Pump cooling	10	freshwater
	Steam condensate	14	

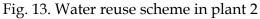
Table 10. Water using operations

Table 11. Limiting water of
water operating data

process	operation	Flow rate	Current water	Limiting inlet
process	operation	Flow rate	source	concentration (mg/l)
perchloravinyl	Alkali solution preparation	5	freshwater	1000
	Absorber	2	freshwater	600
Sodium hypochlorite	Alkali solution preparation	2	freshwater	600
chlorine liquid	Bottle washing	1.5	freshwater	600
	Hot water tank	3.5	freshwater	450
hydrochloride	absorber	20	freshwater	600
chlorinated paraffin	Tail gas absorption	6	freshwater	600
White carbon black	absorber	10	freshwater	450
	Acid gas absorption	6	freshwater	450
	Tail gas absorption	6	freshwater	450
	Gas cooling	5	freshwater	450
electrostenolysis	Electrostenolysis tank	40	Pure water	0
	Resin regeneration	15	Pure water	0
	Pump sealing	7.5	Pure water	0
Bleaching powder	Pump sealing	10	freshwater	450
	Recycle supplement	20	freshwater	1000
	Cooling tower supply	26	freshwater	500
	washing	10	freshwater	
Salt dissolving	brine sludge washing	10	freshwater	450
	Salt dissolving	15	Resin regeneration	100
	Pump cooling	10	freshwater	450
	refining agent preparing	18	freshwater	100
Evaporation	Pump cooling	10	freshwater	450
	Steam condensate	14		0

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contaminants can be excluded. Analyzing the quality control items, the water using operations are sensitive to the PH value and the concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> (total hardness). For example, the water used in hydrochloride absorption cannot be alkaline, and the salt dissolving unit require low concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup>. On the other hand, the wastewater discharge of the operations mainly contains H<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>. Consequently, total hardness is chosen as the chief contaminant that constraints water reuse. PH value is the assistant constraint. The limiting data is shown in table 11.

Step 4. network design

We analyze and optimize the existing system in two aspects: intra-plant integration and inter-plant integration. The design methodology is adopted from Liao et al.<sup>[60]</sup>, and the detailed procedure is omitted here. Figures 12 to 14 represent the obtained intra- and interplant network structures. Note that no reuse happens in plant 3, because plant 3 only consumes pure water which cannot be replaced by freshwater.

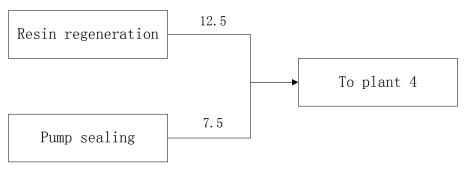


Fig. 14. Cross plant water reuse scheme

#### 4. Conclusion

Due to the water shortage and environmental concerns, it is very important to improve the water using efficiency in traditional chemical industries. We take an chlor-alkali complex as example to show the applicability and effectiveness of the pinch based water integration technology. Based on the balanced system water consumption data, evaluation of the existing system has been established. The analysis and optimization of the whole system are carried out in cooling water system and process water system respectively.

For the cooling water system, the current cooling tower bottleneck has been relaxed by sequential arrangement of the coolers. For the process water allocation system, a number of 13 measures has been proposed (as shown in table 12) to save 88 t/h freshwater. If the following freshwater and wastewater related cost are adopted:

If the following freshwater and	wastewater related
Freshwater cost:	0.4 RMB/t
Pure water cost:	10.00 RMB/t
Circulating cooling water cost:	0.5 RMB/t
Water pumping cost:	0.06 RMB/t
Wastewater discharge cost:	1.20 RMB/t
0	

Then the profit obtained from water saving can be calculated as follows:

1. Circulating cooling water system. The heat load of the cooling tower for chlorine liquid section has been enlarged by sequential arrangement of the cooling system. This enlargement breaks down the cooling water bottleneck of the system. Therefore, 208 t/h of the original direct discharge cooling water is now recycled.

Water saving profit:

$$208 \times (1.2 + 0.06 + 0.4 - 0.5) \times 8000 = 1930(\text{kRMB/Y})$$

2. Process water allocation system. The proposed 12 projects save freshwater in the amount of 88t/h. Water saving profit:

 $88 \times (1.2 + 0.06 + 0.4) \times 8000 = 1169(kRMB/Y)$ 

In conclusion, the total saving is 3,099 kRMB per year.

Process (section)	Water flow rate(t/h)	measures	Water saving amount(t/h)
pump cooling(salt dissolving)	10	sent to refining agent preparing	10
pump cooling(evaporation)	10	sent to brine sludge washing	10
Steam condensate (evaporation)	14	sent to salt dissolving	14
absorber(white carbon black)	10	sent to hydrochloride absorber	10
Acid gas absorber(white carbon black)	6	sent to hydrochloride absorber	4
Gas cooling (white carbon black)	5	sent to sodium hypochlorite section	2
		sent to bottle washing	1.5
		sent to hot water tank	3.5
pump cooling (chlorine liquid)	42.4	sent to the absorber in perchloravinyl section	2
Inte	CI	sent to the alkali solution preparation in perchloravinyl section	5
Resin regeneration(electrostenolysis)	15	sent to the bleaching powder section	12.5
Pump sealing(electrostenolysis)	7.5	sent to the bleaching powder section	7.5
Steam condensate (Solid caustic soda)	6	Sent to the hot water tank in the perchloravinyl section	6
total			88

Table 12. List of the retrofit projects

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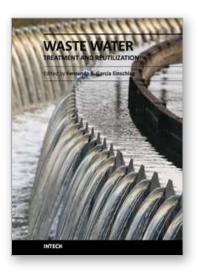
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Waste Water - Treatment and Reutilization Edited by Prof. Fernando SebastiÃin GarcÃa Einschlag

ISBN 978-953-307-249-4 Hard cover, 434 pages **Publisher** InTech **Published online** 01, April, 2011 **Published in print edition** April, 2011

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