Pinch Analysis to an Efficient Management of Water and Effluents in PAD plant

Vanessa Gomes

Instituto Superior Técnico

Abstract

The present study describes the application of water pinch analysis to minimise global fresh water consumption and effluent production in the aniline and derivatives plant of CUF-Químicos Industriais industry. The first step is data extraction, which includes the identification, quantification and characterization of process water streams. Several studies, water mass balances and chemical analysis were carried out to enable the characterization of the process sinks and sources.

A water pinch technique based on water cascade analysis was performed to minimise the use of multiple fresh water sources with multiple contaminants and to design the water network. Different scenarios were studied accomplishing reductions in operational costs in 15%, corresponding to a pay-back time of one year. The introduction of a regeneration unit, reverse osmosis, would provide further reduction up to 48% in operational costs, with a pay-back time less than one year.

1. Introduction

Chemical industries are characterized by the use of important amounts of material and energy resources. To improve sustainability and competitiveness, process industries are increasingly committed to material conservation, for instance using process integration methodologies. These were, firstly, addressed to the synthesis of heat exchanger networks[1], and later, Wang and Smith [2] introduced a wastewater minimisation technique. Nowadays, resource conservation networks synthesis has expanded to the optimum use of various material resources, such as utility gases (e.g., hydrogen and nitrogen), solvent, paper, etc. There are two distinct process integration approaches: pinch analysis and mathematical optimization[3].

The Water management hierarchy was introduced by Wan Alwi *et al.* [4] as a guide for water minimisation. Water management hierarchy consists of five levels. Source elimination (level 1) might be accomplished replacing water with air as a cooling media. Sometimes this is not conceivable and, therefore, an attempt should be made on reduction (level 2). When the first two levels are not possible to implement, reuse and outsourcing (level 3) and regeneration (level 4) should be considered. The aim of water pinch analysis is to maximise water reuse, enabling the decrease of fresh water consumption and wastewater generation. Direct reuse consists in utilizing an operational effluent directly in another one, but it might require adding freshwater or mixing different processes' effluents[2]. Outsourcing involves the use of available external water sources e.g. rainwater or river water, minimizing the fresh water amount needed. However, wastewater can be regenerated by partial treatment to remove key contaminants or reduce its concentration, allowing its supply to other process, named regeneration reuse, or its supply to its original source, named regeneration recycling[2]. The level 5 corresponds to the utilization of freshwater, which should be minimised[4].

Water pinch analysis (WPA) can be defined as a systematic technique of implementing water minimisation strategy through integration of processes for maximum water efficiency[5]. It proposes a reduction of wastewater through reutilization, leading consequently to less pure water flowrate required in a process. WPA involves the following key steps[6]:

a) Analysis of water network;
b) Data extraction;
c) Setting the minimum utility targets;
d) Water network design/retrofit;
e) Economic evaluation.

Several techniques have been developed in the last two decades regarding the identification of the minimum water consumption for a given water network.

The methodology proposed by Wang and Smith[2], called limiting composite curve, is suitable for mass transfer operations. These are operations that include the transfer of certain impurities from a rich stream to the water stream. For each operation, the process streams' concentrations are specified and the maximum inlet and outlet contaminant concentration in the water source must be defined in order to minimise its use. The pinch point is the point where the limiting composite curves touches the water supply line, and the minimum fresh water needed is the inverse of this line's slope. However, there are many water using operations in which water is not a mass transfer agent and so, this methodology is not applied in this case. To overcome these limitations, Dhole *et al.*[7] presented an alternative method, the source and sink composite curves. When a pinch point is obtained, it may be eliminated mixing water streams and then the total freshwater needed is reduced, which is not a systematic method.

To overcome this limitation, a set of rules for sequencing mixing and recycle were proposed[8]. These design rules are based in a key principle: freshwater use is minimised when the contaminant uptake of the water demand is maximised. The final network can involve a lot of mixing streams, which is undesirable in terms of safety, operability and capital cost. This complexity should be reduced, increasing slightly the freshwater flowrate.

Hallale [9] proposed a new approach based on the surplus concept introduced for hydrogen networks[10]. The source and demand composite curves are plotted, with purity being the y-axis and flowrate the x-axis, allowing the identification of the surplus or deficit of pure water areas. Then, the surplus flowrates are plotted in the surplus diagram and the minimum freshwater flowrate for a given process is the one that causes the water surplus diagram to only touch the y-axis, corresponding to the pinch point. This is determined by repeating the procedure for different freshwater flowrates. Process modifications are effective in the region above the pinch point by increasing the flowrate or water purity requirements of a demand. A way to achieve this is the introduction of a regeneration unit to partially treat water sources above the pinch point.

The material recovery pinch diagram is another method to represent the source and sink composite curves[11]. If a sink requires the use of a fresh source, the inlet composition and pollutant load of the sink should be maximized. The use of a source must be maximized until it is fully consumed before maximizing the use of the next source in ascending order of composition.

Water cascade analysis, introduced by Manan *et al.* [5] is a numerical alternative to the graphical water surplus diagram. The minimum freshwater is determined based on the surplus concept but with this technique the iterative steps of the water surplus diagram are eliminated.

Although Prakash and Shenoy[12] presented a new minimum freshwater targeting approach, the composite curves are similar to the ones developed before[11]. The innovation of this work lies in the network design based on the principle of nearest neighbours. The principle of nearest neighbours may be stated as: “To satisfy a particular water demand, the source streams to be chosen are the nearest available neighbours to the demand in terms of contaminant concentration.” According to this, an algorithm was established, in which the first demand to be satisfied is the most restricted one, using its neighbour sources, starting with the cleanest one, and then adding fresh water if the flowrate requirement was not met yet. This design method not only accomplishes the minimum freshwater target but also contributes to minimise the total water flowing through process units, and therefore the network capital cost.

Graphical methods suitable for multiple contaminant problems were presented over the years. One approach is the application of the surplus diagram for each contaminant[13], enabling the determination of the minimum water flowrate. Another method is the application of the nearest neighbours algorithm for this type of problems[14]. Given a problem with more than one contaminant, the nearest neighbours for each sink are the combination of the neighbours for each contaminant. The sinks and sources are rearranged based on their nearest neighbours' concentration and the first sink being satisfied is the less restricted one. Maximising the use of the more polluted water sources, the freshwater flowrate is minimised.

Later, the material recovery pinch diagram[15] and the water cascade analysis[16] were adapted to minimize the use of multiple fresh sources. Multiple water feeds with different concentrations may be available in an industrial plant and can be used to reduce the consumption of the purest freshwater, that is often more expensive. The goal is to maximise the use of the impure water sources, leading to the minimisation of freshwater. A material cascade software[17], suitable for water minimisation, gas recovery and property integration, developed in VBA, for three multiple fresh sources and one contaminant was also presented.

Regarding batch and semi-continuous processes, apart from quality constraint, time dimension is another constraint that needs to be considered. It was initially thought that the application of pinch techniques in batch processes would have very limited benefits due to the reduced flexibility that characterizes non continuous processes and also their intrinsic variations that may lead to deviations from predetermined schedules[18]. There are two possible approaches for this type of problems which are installing, or not, storage tanks. In both of them, the first step is the definition of time intervals based on start and end times of the process sinks and sources.

2. Data Extraction

The first objective in a water pinch analysis is to analyse the current water network and extract the data to allow its quantification and characterization. This is the starting point to a correct identification of the process sinks and sources.

In the PAD plant at CUF-QI, it is manufactured nitric acid (NIT), nitrobenzene (MNB), aniline (ANL), sulphanilic acid (SULF), cyclohexilamine

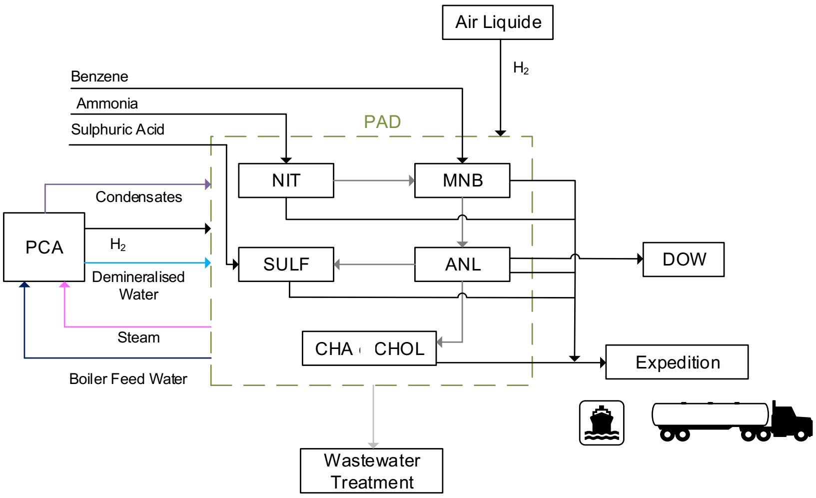

Figure 1: PAD plant and its interactions

and cyclohexanol (CHA CHOL). The interactions between these productions, the chlor-alkali plant, the suppliers and the clients are illustrated in Figure 1.

The PAD plant is outlined in Figure 2, that also shows the three freshwaters' networks available: raw water, demineralized water and boiler feed water. Each network was studied in order to identify all possible uses and flowmeters' location. CUF-QI has a river water caption and after treatment, the raw water is conducted to all plants in the industrial complex. There is not a raw water flowmeter at the entrance of the PAD plant and the only measured utilisations are the cooling towers' make-up and the named raw freshwater network, that is used mostly for washing in all production areas. Demineralised water comes from the nearby chlor-alkali plant of CUF. Boiler feed water is produced in the PAD plant, feeds the boilers and it is also used in the production areas. These two uses are measured *in situ* by total flowmeters ($M1_F$ and $G4_F$).

The make-up of the cooling towers of ANL and MNB use raw water, but also reused water streams, particularly NIT cooling tower's purge. ANL cooling tower also accepts the excess of condensates from V152 and a water stream from sulphanilic acid's crystallisation. These reutilised water flowrates are not measured locally, so it was necessary to estimate them experimentally.

V152 is the last flash unit present in ANL production. It is fed with condensates from other flash units, condensates from two heat exchangers and with a reused water stream from ANL water stripping columns. This later corresponds to an integration already existing in the process and is possible to reuse if its organic concentration is below the specified limit and the solids were separated in the upstream centrifuge and filters. When the required V152's flowrate is not accomplished with these streams, boiler feed water is used through a level control valve. The boiler feed water's flowrate and condensates' excess were estimated using a determined experimental valve's curve.

The same procedure was performed to obtain the demineralised water's flowrate added to tank 120-012 in MNB production. This flowrate is determined by two valves, a level valve and an on-off valve controlled in cascade.

After the identification of freshwaters' utilisations and effluents' production, it was necessary to define the limiting concentrations of the sinks. It was determined that all sulphanilic acid production's effluents would not be reused.

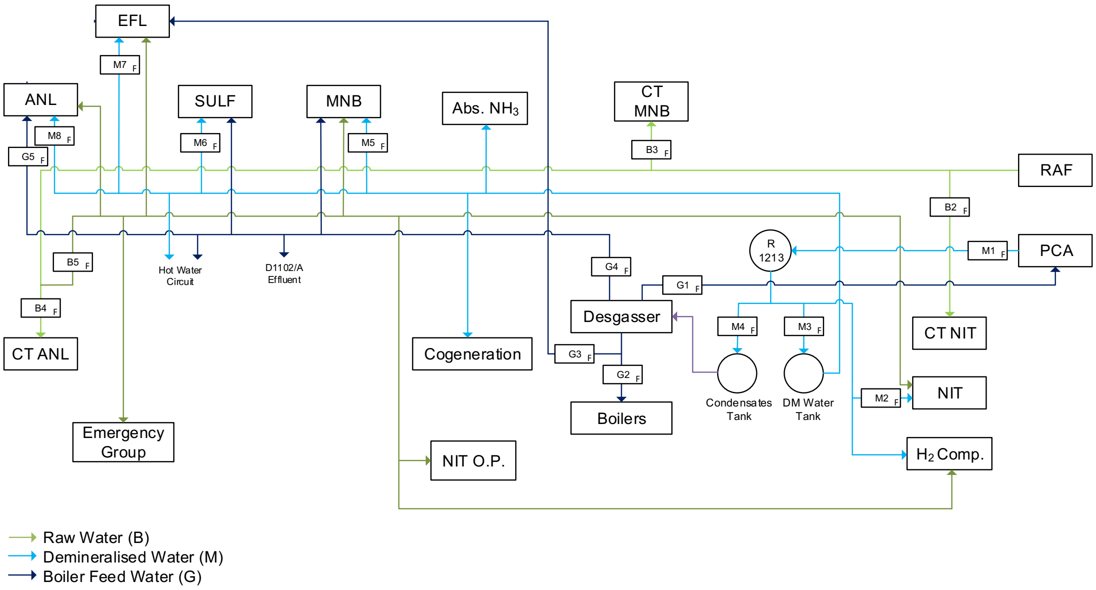

Figure 2: Freshwaters' networks

The identified process sinks are:

1. The three cooling towers' make up flowrates;
2. Demineralised water used in vacuum group and with the catalyst in ANL production;
3. Utilisation of boiler feed water in V152;
4. Demineralised water added to tank 120-012 and to the ammonia scrubber in MNB production;
5. Demineralised water used in nitrophenol reconcentration.

The process sources are:

1. Effluent from the aqueous effluent pond in NIT production;
2. Effluent from the ANL stripping columns when not possible to reuse in V152;
3. Effluent from MNB stripping column and from the MNB washing stage;
4. ANL e MNB cooling towers' purges;
5. Boiler purge.

Table 1 shows the listed sinks and sources' flowrates and the flowrates of the current integrations implemented in the PAD plant.

The extracted data was obtained between July 2016 to July 2017. Some process modifications, leading to a significant decrease in freshwater's consumption, were executed from September 2016 to February 2017. Then, it was defined that the methodology would be applied to the data corresponding to March 2017. This was the month with the minor deviation between the total inputs and outputs in PAD's global water mass balance. Sinks' characteristics are obtained from lab analysis carried out in the plant for this month, along with others exceptionally requested for this work. Sources' limit concentrations were defined based on the experience of the process engineers, knowing the function of the freshwater in each utilisation.

3. Methodology

A pinch based technique applicable to PAD processes was developed. Water, in PAD plant, is used in cooling, washing, as reactant and as a reaction product. As stated, there are three types of freshwater available in PAD plant, raw water, demineralized water and boiler feed water, so it is important to apply a technique that is capable of minimising them, along with the final wastewater flowrate. Simultaneously, the chosen approach must consider the concentration of more than one contaminant. Pinch based methodologies described in the introduction section are not suitable for this problem or are not available for utilisation. Therefore, it was required to combine two approaches, leading to freshwater and wastewater minimisation and also to the network design. The first step is the utilisation of the RCNet software[17] to determine the flowrates of the freshwaters, for each contaminant. Secondly is the network design, with RCNet software, for the contaminant with higher freshwater flowrate. The third step is the network arrangement, to respect every contaminant maximum concentration. To accomplish this, Excel's solver tool was used, to minimise the operation costs (freshwaters consumption and wastewater disposal).

This approach was tested with literature examples. The minimum flowrates achieved are equal to the ones using the respective paper's methodology. However, the network design was not always the same, but this may be accepted since network design is a degenerated problem[19], especially in the region above the pinch. The networks' differences lie in the diverse way of approaching the problem: the present technique approaches the problem in ascending order of concentration. On the contrary, the nearest neighbours for multiple contaminants[14], addresses the problem from the less restricted sink to the highest one.

Two contaminants, based on PAD processes' characteristics, were chosen to perform pinch analysis: chloride concentration, mostly because of cooling water's specification in the nitric acid production, and total organic carbon, because of the products formed in this industrial plant.

Some integrations were restricted in the application of this methodology, due to the presence of other contaminants or other characteristics not accounted.

4. Results

Several scenarios, with and without the implementation of a regeneration unit, were analysed in order to better understand which integrations may be executed.

Demineralised water and boiler feed water present the same chloride concentration. The main difference between them is their temperature. Then, in the present study, it is only considered demineralised water as a freshwater, being the use of boiler feed water analysed subsequentially.

Results were studied through an economical evaluation that considers the possible savings in operation costs and the necessary piping investment to accomplish them.

Initially, a scenario was studied in which only the sources currently being sent to wastewater were considered and the sinks were the freshwater flowrates consumed. ANL and MNB cooling towers were not considered as sinks due to their cooling water specification. The use of NIT cooling tower's purge (E1) in the make-up of these towers, causes their cooling water being close to the specified limits. Thereby only raw water can be used to satisfy the remaining make-up flowrates. The effluent from water stripping columns (A1) was not considered as a water source, due to a high organic concentration or presence of solids. Seven integration projects were obtained, decreasing the operation costs in only 3%. In addition, the whole scenario presented a payback time higher than five years, which is not profitable. This result was expected since many restrictions were imposed.

To obtain a new perspective, another scenario was studied including all sinks and sources presented in Table 1.

Table 1: Flowrates of freshwater, effluents and current integrations implemented (marked in green)

	NITCT	GV	V152	Catal.	ANLCT	Scrubber	120-012	MNBCT	ConcNTF	WW	FW
DW		0,08	4,36	0,0016		0,08	0,068		0,124		4,71
RW	21,04				11,96			3,00			36,0
E1					4,44			2,96			
E2										1,64	
E3										3,48	
E5										0,052	
A1			1,88							3,60	
E7										5,4	
E8										0,284	
E12					0,068					0	
E13										0,116	
C3					0,37					0	
Total	21,04	0,08	6,24	0,0016	16,84	0,08	0,068	5,96	0,124	14,57	

Table 2: Integration projects' flowrates obtained in the last studied scenario. Grey cells represent the restricted integrations

	NITCT	GV	V152	Catal.	ANLCT	Scrubber	120-012	MNBCT	Conc NTF	WW
DM			2,14	0,0016						
AB	21,04				3,31		0,068	5,96		
E5			▨		0,05					0
A1			3,98	▨		▨	▨			1,5
E8	▨	▨	▨	▨	▨		▨	▨		0,284
E13			0,12	▨						0
E15					13,48					0
C3		0,08	▨			0,08	▨		0,124	0,088
Total	21,04	0,08	6,24	0,0016	16,84	0,08	0,068	5,96	0,124	

Some interesting conclusions were achieved. The present methodology suggested the use of NIT cooling tower's purge (E1) in the ANL e MNB cooling towers and the use of water stripping columns' effluent (A1) in flash V152, as it is done at present. However, in order to fulfil sinks' limit concentrations, these two sources were not completely used. Other integration projects concerning the remaining sinks were obtained. The result lead to a 15% reduction in the operation costs over the current operation costs. Implementing all integration projects proposed, the investment payback time is one year.

It is known that regeneration units lead to a freshwater flowrate minimisation. In the present work, the introduction of a reverse osmosis unit to regenerate cooling towers' purges (E1, E2, E3) and the effluent from the water stripping column in the MNB production (E7) was studied. It was determined that the reverse osmosis unit removes 80% of the initial chloride and nitrate concentrations and it is possible to reuse 75% of the initial flowrate. The regenerated water stream (E15) was the one used in the methodology application. The proposed network is shown in Table 2.

Investing in a reverse osmosis unit enables a 48% reduction in operation costs (freshwater and wastewater disposal), with a payback time of ten months. The freshwater used to satisfy V152 unit is boiler feed water, as in the current situation.

Table 3 shows the results' summary of these three studied scenarios and a comparison with the current situation.

5. Conclusions

During data extraction, it was observed that some water streams flowrates are not measured *in situ*. It is recognized that the measurement of total freshwater used in each production plant is a way to sign unnecessary uses and rupture identification.

Table 3: Results' summary

	Present Scenario	Scenario 1	Scenario 2	Scenario 3
Demineralised water flowrate	4,71	4,31	2,15	2,15
Raw water flowrate	36,0	35,9	36,3	30,4
Wastewater flowrate	14,6	14,1	12,4	6,4
Pay-back time (year)	-	5,6	1	0,8

A relevant conclusion regarding the effluent's integrations already implement was achieved. The integrations carried out at present are the best solution, according to the methodology used in this study. However it is essential to be aware that the cooling water of ANL and MNB production are close to the specified limits. The methodology does not allow the full utilisation of the water stripping columns' effluent in the unit V152 due to the imposed chloride concentration limit. These two situations must be taken into account in a near future.

As referred, the installation of a new regeneration unit, despite its initial investment, presented a payback time minor than one year, being this the best result achieved. Therefore, it is possible to state that the introduction of a reverse osmosis should be considered in the CUF PAD plant. A detailed design of this unit is out of the scope of the present work, but it must be performed to ensure its efficiency.

6. Literature Cited

1. Linnhoff, B. and E. Hindmarsh, *The Pinch Design Method of Heat Exchanger Networks.* Chemical Engineering Science, 1983. **38**: p. 745-763.
2. Wang, Y.P. and R. Smith, *Wastewater Minimisation.* Chemical Engineering Science, 1994. **49**: p. 981–1006.
3. Foo, D.C.Y., *Process Integration for Resource Conservation*, ed. S. Lee. 2012, Boca Raton, FL, USA: CRC Press.
4. Wan Alwi, S.R.*, et al.*, *Systematic Design of a Maximum Water Recovery Network for an Urban System Based on Pinch Analysis.* The Institution of Engineers, 2006. **67**(1): p. 57-64.
5. Manan, Z.A.*, et al.*, *Targeting the Minimum Water Flow Rate Using Water Cascade Analysis Technique.* AIChE Journal, 2004. **50**(12): p. 3169-3183.
6. Wan Alwi, S.R. and Z.A. Manan, *Water Pinch Analysis for Water Management and Minimisation: An Introduction*, in *Process Integration Handbook*, Klemes, Editor. 2013, Woodhead Publishing: Cambridge, UK. p. 353-382.
7. Dhole, V.R.*, et al.*, *Make Your Process Water Pay for Itself.* Chemical Engineering, 1996. **103**: p. 100-103.
8. Polley, G.T. and H.L. Polley, *Design Better Water Networks.* Chemical Engineering Progress, 2000. **96**(2): p. 47-52.
9. Hallale, N., *A New Graphical Targeting Method for Water Minimisation.* Advances in Environmental Research, 2002. **6**(3): p. 377–390.
10. Alves, J.J., *Design and Analysis of Refinery Hydrogen Distribution Systems*. 1999, UMIST.
11. El-Halwagi, M.M.*, et al.*, *Rigorous Graphical Targeting for Resource Conservation via Material Recycle/Reuse Networks.* Industrial & Engineering Chemistry Research, 2003. **42**: p. 4319–4328.
12. Prakash, R. and U.V. Shenoy, *Targeting and Design of Water Networks for Fixed Flowrate and Fixed Contaminant Load Operations.* Chemical Engineering Science, 2005. **60**(1): p. 255-268.
13. Zhao, Z.*, et al.*, *The Integration of the Hydrogen Distribution System with Multiple Impurities.* Chemical Engineering Research and Design, 2007. **85**(9): p. 1295-1304.
14. Zhang, Q.*, et al.*, *Evolutionary Graphical Approach for Simultaneous Targeting and Design of Resource Conservation Networks with Multiple Contaminants.* Industrial & Engineering Chemistry Research, 2013. **52**(3): p. 1309-1321.
15. Wan Alwi, S.R. and Z.A. Manan, *Targeting Multiple Water Utilities Using Composite Curves.* Industrial & Engineering Chemistry Research, 2007. **46**: p. 5968–5976.
16. Foo, D.C.Y., *Water Cascade Analysis for Single and Multiple Impure Fresh Water Feed.* Chemical Engineering Research and Design, 2007. **85**(8): p. 1169-1177.
17. Ng, D.K.S.*, et al.*, *RCNet: An Optimisation Software for the Synthesis of Resource Conservation Networks.* Process Safety and Environmental Protection, 2014. **92**(6): p. 917-928.
18. Majozi, T.*, et al.*, *A Graphical Technique for Wastewater Minimisation in Batch Processes.* Journal of Environmental Management, 2006. **78**(4): p. 317-329.
19. Foo, D.C.Y., *State-of-the-Art Review of Pinch Analysis Techniques for Water Network Synthesis.* Industrial & Engineering Chemistry Research, 2009. **48**(11): p. 5125–5159.