# Investigation of Opportunity for Waste Water Minimization in Petroleum Refinery Using Pinch Technology

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Abstract: Waste water generation in the petroleum refineries and the stringent environmental disposal regulations have called for an intensive waste water management. This study is aimed at finding appropriate way of minimizing waste water generation in the refineries. For this purpose, a typical refinery which utilizes 40.5 te/hr of fresh water in its three basic operations (Distillation, Hydrodesulphurizer and Desalter) was chosen and studied based on single and multiple containment approaches. These methods established that the amount of fresh water required for an operation in the refinery is dependent on the mass transfer of the chosen key reference contaminant. Three key containments, namely  $H_2S$ , oil and suspended solids where chosen and analysed. The study achieved the aim of simultaneously minimizing both the fresh water consumption and the effluent waste water generation via maximization of the internal water reuse in the operations. The results showed that there is about 37% and 15.4% reduction in waste water generation based on the single and multiple contaminant approaches respectively. The tools applied here are based on the principle of mass transfer.

Keywords: Waste Water Generation, Petroleum Refineries, Stringent Environmental.

# 1. INTRODUCTION

The current drive towards environmental sustainability and the rising cost of fresh water and effluent treatment have encouraged the process industries to find new and efficient ways of reducing the fresh water consumption and waste water generation. Petroleum refineries and other process plants are now searching for more serious measures to tackle these problems by minimization of fresh water consumption through in-plant reuse and recycles. The direct consequence of this measure is a reduction in effluent generation as a means to reduce production cost and also to ensure sustainable growth in the business environment.

Several methodologies have been proposed to design economical waste water minimisation techniques; one of these approaches is the development of a systematic method to the design water recovery network aimed at the minimizing freshwater and waste water requirement for the process industry [11]

One of the methods used in achieving this sustainable environmental friendly and cleaner production is the application of water pinch technology. Pinch technology is a rigorous structured approach that has been used to tackle a wide range of problems related to processes and site utility. This involves opportunities such as capital investment planning efficient improvement and cost reduction [4].

The success of pinch technology is due to the fact that the technology analyses a commodity on the basis of both equality and quantity as the cost of a process is a function of both in general, process uses high value utilities and reject waste at lower value. Thus, in the case of water, pure water is fed to the process and contaminated waste water is rejected to the treatment plants.

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Water pinch technology is a type of mass exchange integration between water using operations. It enables practicing Engineers to answer a number of important questions when retrofitting existing facilities and designing new water-using networks. The technology incorporates graphical analysis for setting targets and realizing the design of the network. When designing the network, individual demand for a commodity is matched with a suitable supply equality. Through maximization of the match between demand and supply, the importation utility is in the other hand minimized.

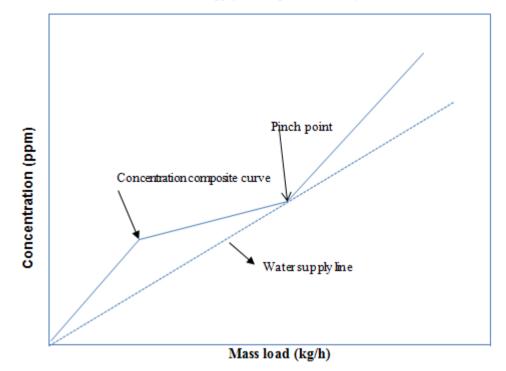


Figure1: Composite curve to determine Freshwater Pinch Concentration [16]

There are two main approaches generally used to address the issue of systematic synthesis of water recovery network of the process industries namely,

- 1. Graphical approach (water pinch technology)
- 2. Mathematically based optimization approach

These method are based on mass exchange of one several contaminants [2]. When a problem is based on a single contaminant, which are being transferred at the same time, the problem is solved using multiple contaminant approach. Mathematical and graphical methods can be used in both cases, but each method has its advantages and disadvantages. The graphical methods are more practical to solve single contaminant problems but sometimes it become complicated or even impossible on multiple contaminants problems [1], [3], [9].

The graphical divides the synthesis task into a two-step procedure that is utility targeting and network design. The advantage of this method is that the maximum utility targets are located ahead of the detailed design of the network [5].

Wang and Smith applied the water pinch technology on a generalized mass exchange network synthesis (MENS)[16]. The basic concept in their approach was the treatment of water using operation as mass exchange problems. They introduced the concept of limiting water profile, concentration composite curve and concentration internal diagram to determine the fresh water – pinch concentration. The graphical approach was then used to calculate the maximum fresh water flowrate of the system. Though, they late explored the opportunity of regeneration – reuse, Regeneration-recycle in their latter work. They also considered flowrate constraints in their network analysis.

Mann and Liu showed in their work by graphical method that when regeneration was applied, the system presented a regenerated water pinch concentration which can be different from fresh water pinch water concentration [10]. Hallale showed that fresh water pinch can be equal or less than regenerated water pinch[8]. Against these odds, Castro proposed a procedure in which the minimum fresh water consumption and the mass exchange network synthesis were attained simultaneously based on interval concentration [6].

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## 2. CASE STUDY

The design in this work is based on the method of [16] and [10]. The method is applied to minimize waste water (effluent) generation and fresh water consumption in a petroleum refinery. The Refinery case study currently utilities 40.5te/h of fresh water in the three major operations (steam stripping, Hydrodesulphurizer and Desalter) under consideration. Here three main contaminants  $H_2S$ , oil and suspended solid are considered as show in Table 1. The constraints and the stream flowrates were necessary to achieve mass exchange of contaminants [15],[12],[13]. The two approaches for waste water minimization were used with the assumption that there is no water loss in the process also the mass transfer assumption that the removal of one contaminant can lead to the removal of other contaminants in same ratio was used.

Operation	Flowrate(te/hr)	Contaminant	Concentration in (ppm)	Concentration out (ppm)
Distillation	6.60	H2S	0	320
(steam stripping)		Oil	0	15
		S.S	0	15
Hydrodesulphurization	3.45	H2S	200	1200
unit (HDS)		Oil	20	120
		S.S	40	66
Desalter	30.00	H2S	15	40
		Oil	10	100
		S.S	20	95
Total	40.05			

 Table1 The Limiting Process Data for the Refinery

### 3. RESULTS AND DISCUSSION

The problem was treated as a single contaminant system by taking  $H_2S$  as the reference contaminant, the Fresh water pinch was obtained as 25.3te/h, which translated to 37% reduction of waste water generation as shown in figure 2. The same problem was treated as multiple contaminant system, having taken operation 1 and contaminant  $H_2s$  as the reference operation and the reference contaminant respectively, it was observed that the concentration of  $H_2S$  in operation (1) could not allow the water to be reused in operation (2) also from the outlet of operations (2) and (3) as show in figure 2. it was observed that both streams cannot be reused in any operation, hence the only opportunity available for water reuse was to reuse water from operation (1) at a certain point in operation (2) (above the inlet) as show in figure 4 and 5. But with further study there was an opportunity for further saving of fresh water by the application of the pinch interval water reused at a certain point in operation (3) as shown in figure 4 and 5 which led to a new pinch of 33.87te/h of fresh water and it is translated to a total of 15.4% reduction in the volume of waste water generated.

From this result, it was evident that the process of waste water reuse using single contaminant gave a higher level of fresh water reduction as compared to multiple contaminant approach. Hence there is an opportunity to save 143.6 million naira and 60.2 million naira in the annual operating cost based on the single and multiple contaminant approaches respectively.

Table 2 Concentration	Interval Diagram	for H <sub>2</sub> S
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Concentration (ppm)	1	2	Operation 3 30.00 te/hr	(kg/hr)	Cumulative Mass load (kg/hr)	
0.00	<b>↑</b>			0.00	0.00	0.00
15.00			1	0.10	0.10	6.56
40.00			I	0.91	1.01	25.31
200.00		1		1.05	2.06	10.31
320.00				1.20	3.26	10.20
1200.00				3.04	6.30	5.25

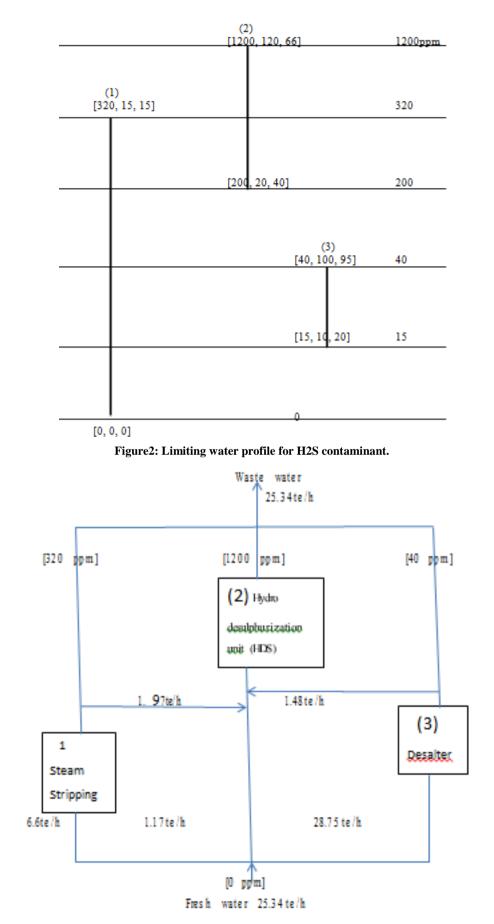


Figure 3: Block Diagram of the Simplified Water Network for single Contaminant

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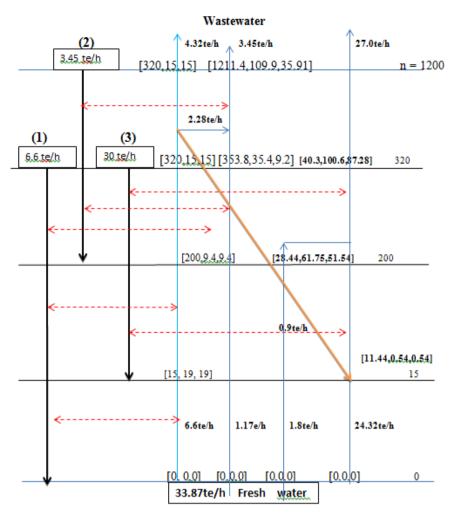


Figure 4: Water Network for the Multiple Contaminants Problem with Pinch Interval Water Reuse.

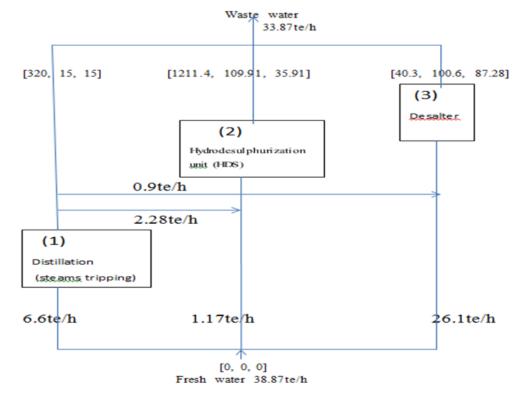


Figure 5: Block Diagram of the Simplified Water Network using Pinch Interval-water reuse

Utility	Operating Cost( <del>N</del> /te)	Original Utility Flow (te/h)	Pinch solution Utility Flow (te/h)	Change %	Difference (te/h)	Differential Cost ( <del>N</del> /h)	Original Cost ( <del>N</del> /h)
Fresh Water	850 *	40.05	25.3	-37.0	-14.75	-125.37.50	34,042.5
Effluent Discharge							
Charges	20.5 **	40.05	25.3	-37.0	-14.75	-302.38	821.03
Effluent Water							
<b>Treatment Cost</b>	256.5 **	40.05	25.3	-37.0	-14.75	-3,783.38	10,272.83
Total Forecast						-16,623.26	45,136.36
Cost							

 Table 3A Cost Flow Rate Comparison for Before and After Pinch Analysis (Single Contaminant)

 Table 3B Cost Flow Rate Comparison for Before and After Pinch Analysis (Multiple Contaminant)

Utility	Operating Cost( <del>N</del> /te)	Original Utility Flow (te/h)	Pinch solution Utility Flow (te/h)	Change %	Difference (te/h)	Differential Cost ( <del>N</del> /h)	Original Cost ( <del>N</del> /h)
Fresh Water	850 *	40.05	33.87	-15.4	6.18	-5,253.00	34,042.5
Effluent Discharge Charges	20.5 **	40.05	33.87	-15.4	6.18	-126.69	821.03
Effluent Water Treatment Cost	256.5 **	40.05	33.87	-15.4	6.18	-1,585.17	10,272.83
Total Forecast Cost						-6,964.86	45,136.36

\*Akwa Ibom State Water Company

\*\* [15]

Note: All costs are in Nigerian naira.

# 4. CONCLUSION

This paper shows how resource conservation can be handled efficiently through the process of pinch analysis, by setting the minimum fresh resources and waste targets in prior, engineers can now identify the maximum possible saving that can be achieved in reuse/recycle systems. Hence, waste water minimization through pinch analysis is a powerful tool in process integration.

The result of the single contaminant approach was more considerable, but the water minimization through the multiple contaminant results proved to be more precise. The result obtained compare favourably with similar work carried out by other researchers. [14] used Double contaminant approach and obtained 42% reduction. Hence, it is suggested that more contaminants should be considered for any study of water network design as it will help to achieving product quality and in abating equipment fouling.

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#### **APPENDIX - A**

#### Calculation for Minimum Fresh Water Requirement for Multiple Contaminant Problem:

#### Step1

From the first interval boundary, operation (1) is the only operation existing hence  $\Theta_{1,1}$  is given as

$$\theta_{1.1} = \text{Max} \left\{ \begin{array}{c} (15-0), (1.9-0), (1.9-0) \\ \hline 15 & \hline 1.9 & \hline 1.9 \end{array} \right\}$$

$$= \text{Max} [1.1.1] = 1$$

The fresh water requirement of operation 1 at the first concentration interval boundary and the flowrate available for reuse at the next interval from equation (3.24)

$$\mathbf{F}_{1.1} = \mathbf{\theta}_{1.1} \mathbf{f}_1 = \mathbf{T}_{1.1}$$

 $= T_{1.2} = 1. (6.6 \text{te/h})$ 

The available water for reuse at the second concentration interval boundary

$$\begin{split} W_{1.H2S,2} &= 0ppm + (6.6te/hr(15-0)ppm)/(6.6te/hr) = 15ppm \\ W_{1.oil,2} &= 0ppm + (6.6te/hr(1.9-0)ppm)/(6.6te/hr) = 1.9ppm \\ W_{1.S,S,2} &= 0ppm + (6.6te/hr(1.9-0)ppm)/(6.6te/hr) = 1.9ppm \end{split}$$

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## Step2

This is at the second concentration interval, since no operation has ended at this point,

 $6.6 \text{te/h} + \text{F}_{1.2} = \theta_{1.2} (6.6 \text{te/h})$ 

But,

 $\theta_{1.2} \left[ \frac{(200-15)ppm}{200-\dot{W}1H2S.2}, \frac{(9.4-1.9)ppm}{9.4-\dot{W}1.oil.2}, \frac{(9.4-1.9)ppm}{9.4-\dot{W}1.ss.} \right]$ 

Where

 $\dot{W}_{1.H2S.2} = \frac{(6.6te/h)(15)ppm}{6.6te/h + F1.2}$  $\dot{W}_{1.oil.2} = \frac{(6.6te/h)(1.9)ppm}{6.6te/h + F1.2}$  $\dot{W}_{1.SS,2} = \frac{(6.6te/h)(1.9)ppm}{6.6te/h + F1.2}$ 

Hence on solving the equations together

$$F_{1.2} = 0te/h$$

$$\theta_{1.2} = 1$$

 $\dot{W}_{1,H2S,2} = 15$  ppm,  $\dot{W}_{1,oil,2} = 1.9$  ppm,  $\dot{W}_{1,SS,2} = 1.9$  ppm

Operation 3 has also started at the second concentration interval boundary and must be considered, it required fresh water since no water is available for reuse, evaluating the fresh water requirement of operation3 at the second concentration interval boundary with flow rate of water leaving operation 1 at the pinch interval boundary,  $X_{1,3,2}$ 

$$X_{1.3.2} + F_{3.2} = \theta_{3.2}(30te/hr)$$
  

$$\theta_{3.2} = \text{Max}\left[\frac{(61.44 - 10)}{61.44 - \varpi_{3.oil.2}} \frac{(62.87 - 20)}{62.87 - \varpi_{3.5.5.2}}\right]$$
  

$$\varpi_{3.H2S.2} = \frac{X_{1.3.2} + (320ppm)}{X_{1.3.2} + F_{3.2}}$$
  

$$\varpi_{3.oil.2} = \frac{X_{1.3.2} + (15ppm)}{X_{1.3.2} + F_{3.2}}$$
  

$$\varpi_{3.S.S.2} = \frac{X_{1.3.2} + (15ppm)}{X_{1.3.2} + F_{3.2}}$$
  
On solving all equations

 $X_{1.3.2} = 0.9 te/hr$ 

$$\theta_{3.2} = 0.84$$

 $F_{3,2} = 24.3 te/hr$ 

 $\varpi_{3,H2S,2} = 11.43ppm$ 

 $\varpi_{3.oil.2} = 0.54ppm$ 

$$\varpi_{3.S.S.2} = 0.54ppm$$

The flow rate and concentration for reuse at third concentration interval boundary are

$$T_{3.3} = 0.9 + 24.2 = 25.2 \text{te/hr}$$

$$\begin{split} W_{3.H2S.3} &= 11,\!43ppm + (30te/hr(29.29-15)ppm)/(25.2te/hr) = 28.44ppm \\ W_{3.oil.3} &= 0.54ppm + (30te/hr(61.44-10)ppm)/(25.2te/hr) = 61.78ppm \\ W_{3.S.S.3} &= 0.54ppm + (30te/hr(62.87-20)ppm)/(25.2te/hr) = 51.54ppm \end{split}$$

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#### Step3

Considering all the operations, to calculate the flow rate and the concentration of water leaving the interval boundary 3.the water flowrate through operation 1 is at its limiting flow rate ,hence using  $C_{i,j,4}$  from the limiting water profile,

$$T_{1,4}$$
= 6.6te/hr,  $W_{i,H2S,4}$ =320ppm,  $W_{1,oil,4}$ =15ppm,  $W_{1,SS,4}$ =15ppm

Hence,

$$\theta_{2.3} = \text{Max}\left[\frac{(320 - 200), (32 - 20), (43.12 - 40)}{320}\right]$$

Max (0.34, 0.34, 0.07)

 $F_{2.3} = 0.34(3.45 \text{te/hr}) = 1.17 \text{te/hr}$ 

Operation2 at fourth concentration interval boundary has  $T_{2.4} = 0$ te/hr +1.17te/hr = 1.17te/hr

$$W_{2.H2S.4} = 0ppm + (3.45te/hr(320 - 200)ppm)/(1.17te/hr) = 353.8ppm$$

$$W_{2,oil.4} = 0ppm + (3.45te/hr(32 - 20)ppm)/(1.17te/hr) = 35.38ppm$$

$$W_{2.S.S.4} = 0ppm + (3.45te/hr(43.12 - 40)ppm)/(1.17te/hr) = 9.2ppm$$

The flow rate of operation three is obtained using

$$f_{3.3}^* = T_{3.3} + q_{1.3} + F_{3.3} = \theta_{3.3}f_3$$
$$W_{3.4} = W_{3.j.4} + \frac{f_3(C_{3j4} - C_{3j3})}{T_{3.4}}$$
$$T_{3.4} = F_{3.3} + T_{3.3}\sum_i q_{l3m<3}$$

Hence

$$F_{3.3} = 1.8te/hr$$
  
 $T_{3.3} = 27te/hr$   
 $W_{3.H2S.4} = 40.03ppm$   
 $W_{3.oil.4} = 100.6ppm$   $W_{3.S.S.4} = 87.28ppm$ 

To calculate the fresh water requirement above the pinch and the a concentration of water from operation 2 at the fourth concentration interval boundary,

Step4

Since no fresh water is required above the pinch, the fresh water of operation2 at this point is 0 hence, F<sub>2.4</sub>=0

Water leaving operation1 is reused at this point using

$$F_{2.3} + q_{1.2.4} = \theta_{2.4} \times f_2$$

$$1.17 + q_{1.2.4} = \theta_{2.4} \times 3.45$$

$$\theta_{2.4} = \operatorname{Max} \left[ \frac{(1200 - 320)}{1200 - \varpi_{2.H2S.4}} \frac{(120 - 32)}{120 - \varpi_{2.oil.4}} \frac{(66 - 43.12)}{66 - \varpi_{2.S.2}} \right]$$

$$\varpi_{2.H2S.4} = \frac{\left( \frac{1.17te}{hr} \times 353.8ppm \right) + (q_{1.2.4} \times 320)}{1.17te/hr} + q_{\frac{1.2.4te}{hr}}$$

$$\varpi_{2.oil.4} = \frac{\left( \frac{1.17te/hr}{\chi} \times 353.8ppm \right) + (q_{1.2.4} \times 15)}{1.17te/hr} + q_{1.2.4}te/hr}$$

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 $\varpi_{3.S.S.3} = \frac{\left(\frac{1.17te}{hr} \times 9.2ppm\right) + (q_{1.2.4} \times 15)}{1.17te/hr + \frac{q_{1.2.4}te}{hr}}$ 

Solving all the equation together,

 $\begin{array}{l} q_{1.2.4} = 2.28 te/hr \\ \theta_{2.4} = 1 \\ \overline{w}_{2.H2S.4} = 331.46 ppm \\ \overline{w}_{2.oil.4} = 21.91 ppm \\ \overline{w}_{3.S.S.3} = 13.03 ppm \\ \mbox{At the fifth concentration interval,} \\ W_{2.H2S.5} = 331.46 ppm + (3.45 te/hr(1200 - 320) ppm)/(3.45 te/hr) = 1211.4 ppm \\ W_{2.oil.5} = 29.91 ppm + (3.45 te/hr(120 - 32) ppm)/(3.45 te/hr) = 109.91 ppm \end{array}$ 

 $W_{2.S.S.5} = 13.03ppm + (3.45te/hr(66 - 43.12)ppm)/(3.45te/hr) = 35.91ppm$