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On zero water discharge solutions in the process industry[☆]

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Abstract

This paper presents a mathematical programming approach to analyze the feasibility of zero liquid discharge option in different industries. Mathematical programming methodologies are applied to four industrial cases—a tricresyl phosphate plant, an ethyl chloride plant, a paper mill and a refinery. In each case study various *end of pipe* and regeneration configurations using different treatment technologies are explored to determine the possibility of zero liquid discharge and its economical feasibility. The results show that the relationship between the cost of regeneration and the cost of freshwater as well as the discharge concentration of the treatment is the determining factor for the feasibility of zero liquid discharge.

Keywords: Water management; Zero liquid discharge

1. Introduction

Water is required in several fundamental process operations such as scrubbing, extraction, steam generation, etc. Current practice usually merges several waste streams and utilizes appropriate technologies in series to clean the single stream before disposal. This method is referred to as an *end of pipe* non-distributed wastewater cleanup and the cleanup technologies were discussed thoroughly by Belhateche (1995). Recently, the enforcement of stricter environmental regulations on industrial effluent and sometimes its scarcity and cost have favored a different approach to water usage. In the eighties and nineties, water reuse started to become a popular means to reduce freshwater intake and reduce treatment costs. Additionally, distributing treatment processes among the various polluted streams and even decentralizing is gaining acceptance. This trend towards water reuse and decentralization in some cases may result in economically feasible zero discharge facilities, a concept that refers to closed circuits of water, such that disposal is eliminated.

Advantages and disadvantages of zero discharge facilities are currently being seriously considered and discussed. Zero liquid discharge minimizes the consumption of freshwater to that of make-up; therefore, it should help relieve freshwater availability limitations in places where it is scarce or expensive. In addition, elimination of liquid discharge will obviate the need to comply with increasingly stringent environmental restrictions. Purchased water, and wastewater treatment and disposal costs can be significant; thus, savings associated with minimized site makeup water and wastewater flows can justify capital expenditures to minimize, if not completely eliminate, wastewater flows. Zero liquid discharge can save money on real estate costs in the case of new facility construction, since location near a suitable receiving waterway would not be necessary. In addition, zero liquid discharge helps to gain community trust and support and shows sensitivity to the environment. On the other hand, sometimes the disadvantages of implementing zero liquid discharge include higher operating costs due to treatment of water to the extent it is suitable for reuse, or higher capital cost in retrofit projects due to large scale restructuring

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of piping and the arrangement of the disposal of the solid waste generated. However, in some cases the solid waste generated may be sold which brings in additional revenue in addition to solving disposal problems.

The problem of wastewater reuse has received attention from several researchers. The practice was analyzed first by Prof. Umeda in 1980 (Takama et al., 1980), but the field owes more formal existence to the pioneering work of El-Halwagi and Manousiouthakis (1989) in mass exchange networks. These seminal contributions were picked up by Wang and Smith (1994a) and applied to the particulars of this problem. The list of subsequent work is extensive and can be obtained from a recent review (Bagajewicz, 2000).

Wang and Smith (1994b) also introduced the use of water regeneration, which refers to partial treatment to facilitate further reuse, but they concentrated on systems without recycles of water. Zero discharge, therefore, was excluded. Savelski and Bagajewicz (2001) presented targeting models for overall freshwater minimization, which include regeneration with and without recycles. Results from this paper show that zero liquid discharge is feasible only if regeneration has an outlet concentration that is sufficiently small. Otherwise, recycles might exist, but liquid discharge is not completely eliminated. In addition, after these targeting models are solved, several alternatives can be explored to minimize investment cost since the problem has many solutions with the same freshwater consumption.

This paper builds on these developments and studies the possibility of zero discharge cycles in single and multiple contaminant situations, as well as the intricacies of these structures. The targeting models for single contaminant systems are reviewed, and three single contaminant cases are analyzed: water management in a tricresyl phosphate plant, an ethyl chloride plant, and a paper mill process. Finally, a refinery example, which is a multiple contaminant system, is analyzed. Zero liquid discharge possibility in refineries (multiple contaminant case) is studied using a new iterative procedure, which is an extension of the one presented by Bagajewicz and Rivas (2000). This methodology for multiple contaminant systems is briefly reviewed in this paper and it makes use of necessary optimum and linear conditions resulting in an efficient design procedure that is computationally reliable. The possibility of zero discharge in all these case studies is examined using the available treatment technologies.

2. Problem statement and mathematical models

In this section, the problem of determining the feasibility of zero liquid discharge solution is posed in the framework of mathematical programming.

2.1. Problem statement

Given a set of water-using/water-disposing processes and a set treatment processes, it is desired to determine a network of interconnection of water streams between the processes, and between the processes and the treatment units, so that the overall freshwater consumption is minimized or completely eliminated, while each of the processes receives water of adequate quality.

Since the amount of liquid discharged is the same as the amount of freshwater consumed, the objective of minimizing the overall freshwater consumption, as posed in the problem statement, also minimizes the liquid discharge. Thus, the solution to this problem answers the feasibility of zero liquid discharge.

2.2. Solution procedure

The solution of this problem assumes constant load of contaminants removed in the processes, and limits on inlet and outlet concentrations of contaminants in the same way as it was posed by Wang and Smith (1994a), and later used by Savelski and Bagajewicz (2001), Bagajewicz et al. (1999). The outlet concentration limits account for corrosion, fouling, maximum solubility, etc, while the inlet is set to limit the total flowrate through the processes. Further, different solution procedures for single and multiple contaminant systems are employed, as proposed by Savelski and Bagajewicz (2001) and Bagajewicz et al. (1999), respectively. The former approach uses necessary conditions of optimality while the later makes use of a combinatorial search along with necessary conditions of optimality to solve the problem using linear models. We now describe the mathematical models in detail.

2.3. Procedure for single contaminant systems

Savelski and Bagajewicz (2001) exploit the necessary conditions of optimality, developed by Savelski and Bagajewicz (2000), to obtain the following linear model for single contaminant systems.

$$\left.\begin{array}{ll}
\mathrm{P1}=\min\sum_{j}F_{j}^{w} & \\
\text{s.t.} & \\
F_{j}^{w}+\sum_{i}F_{i,j}-\sum_{k}F_{j,h}-F_{j,\mathrm{out}}=0 & \forall j\in N\\
\sum_{i}F_{i,j}(C_{i,\mathrm{out}}^{\max}-C_{j,\mathrm{in}}^{\max})-F_{j}^{w}C_{j,\mathrm{in}}^{\max}\leqslant 0 & \forall j\in N\\
\sum_{i}F_{i,j}(C_{i,\mathrm{out}}^{\max}-C_{j,\mathrm{out}}^{\max})-F_{j}^{w}C_{j,\mathrm{out}}^{\max}+L_{j}=0 & \forall j\in N\\
F_{j}^{w},F_{i,j},F_{j,h},F_{j,\mathrm{out}}\geqslant 0 &
\end{array}\right\} \quad (1)$$

This single component model is rigorous and has no approximations other than the aforementioned assumptions of constant load and maximum inlet and outlet concentrations. The solution of this problem provides the freshwater consumption as well as inter-process reuse of the wastewater for each process. However, this model does not include any regeneration or treatment process. The effluent water ($F_{j,\mathrm{out}}$) from each of the processes is assumed to merge into one stream, which is treated with appropriate treatment technologies before discharge. This scheme is also called centralized treatment or *end of pipe* treatment. Savelski and Bagajewicz (2001) also showed that this problem usually has several alternative (degenerate) solutions, and provided means of determining which of these solutions minimizes capital cost. Specifically, they proposed a second phase where the objective function minimizes the number of connections or their linear combination, which is a simplified substitute for piping cost, while limiting the freshwater consumption to a targeted value.

Savelski and Bagajewicz (2001) also proposed an extension of (P1) to incorporate decentralized treatment and proved that this new model is also linear. Linearity is achieved by fixing the treated water concentration at the lowest possible value, which minimizes the freshwater requirement. The lower bounds of treated water concentration are obtained from treatment technology limitations. The model is:

$$\left.\begin{array}{ll}
\mathrm{P2} = \min \sum_j F_j^w & \\
\text{s.t.} & \\
F_j^w + \sum_i F_{i,j} + \sum_{k=1}^{T} F_{t_k,j} - \sum_k F_{j,h} - \sum_{k=1}^{T} F_{j,t_k} - F_{j,\mathrm{out}} = 0 & \forall j \in N \\
\sum_i F_{i,j}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{in}}^{\max}) + \sum_{k=1}^{T} F_{t_k,j}(C_{t_k,\mathrm{out}} - C_{j,\mathrm{in}}^{\max}) - F_j^w C_{j,\mathrm{in}}^{\max} \leqslant 0 & \forall j \in N \\
\sum_i F_{i,j}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{out}}^{\max}) + \sum_{k=1}^{T} F_{t_k,j}(C_{t_k,\mathrm{out}} - C_{j,\mathrm{out}}^{\max}) - F_j^w C_{j,\mathrm{out}}^{\max} + L_j = 0 & \forall j \in N \\
\sum_{\forall i} F_{j,t_k} - \sum_{\forall j} F_{t_k,j} \geqslant 0 \quad \forall k \in T & \\
F_j^w, F_{i,j}, F_{j,t_k}, F_{t_k,j}, F_{j,h}, F_{j,\mathrm{out}} \geqslant 0 &
\end{array}\right\} \quad (2)$$

The linear model with regeneration (problem P2), provides a target of freshwater (α), which is obtained from P1. Because multiple solutions featuring the same freshwater consumption are possible, a second phase, minimizing the total cost of regeneration is added, as follows:

$$\left.\begin{array}{l}
\mathrm{P3} = \min\{\text{Regeneration Cost}\} \\
\text{s.t.} \\
\sum_j F_j^w = \alpha \\
\text{Mass and component balance}
\end{array}\right\} \quad (3)$$

In this model, the regeneration cost is directly related to the total flowrate $[a_R \sum_{k=1}^{T} \sum_j F_{j,t_k}]$ or to the total load removed $[a'_R \sum_{k=1}^{T} \sum_j F_{j,t_k}(C_{j,\mathrm{out}}^{\max} - C_{t_k,\mathrm{out}}^{\min})]$. In the latter case the condition $C_{t_k,\mathrm{out}}^{\min} \leqslant C_{j,\mathrm{out}}^{\max}$ is imposed. The above problem allows recycles from one process to another and, therefore, is suitable to identify zero discharge solutions. Nevertheless, Savelski and Bagajewicz (2001) proposed additional constraints that allow the identification of solutions without recycles, which are of no importance in this case because recycles are essential to zero liquid discharge.

The capital cost is minimized in the third phase (Savelski and Bagajewicz, 2001). They introduced binary variable, which represents a possible interconnection, to minimize the total number of inlet, outlet and interconnections between the processes using the targets for freshwater (α) and regeneration cost (β) provided by problems (Eq. (2)) and (Eq. (3)) as follows:

$$\left.\begin{array}{l}
\mathrm{P4} = \min\left\{ \sum_{i,j} Y_{i,j} + \sum_{w,j} Y_{w,j} + \sum_{j,o} Y_{j,o} \right\} \\
\text{s.t.} \\
\sum_j F_j^w = \alpha \\
\text{Regeneration Cost} = \beta \\
\text{Mass and component balances} \\
F_{i,j} - UY_{i,j} \leqslant 0 \quad \forall i \in N,\ \forall j \in N \\
F_j^w - UY_{w,j} \leqslant 0 \quad \forall j \in N \\
F_{j,\mathrm{out}} - UY_{j,o} \leqslant 0 \quad \forall j \in N \\
Y_{i,j}, Y_{w,j}, Y_{j,o} \in \{0,1\}
\end{array}\right\} \quad (4)$$

Summarizing, the hierarchy of models is as follows: the freshwater usage and the total operating cost for single contaminant systems is first obtained by solving problem P1. Next, problems P2, P3 and P4 are solved in sequence to obtain a decentralized treatment scheme. The total operating cost therefore includes freshwater cost, regeneration cost, and final treatment cost before discharge, when it applies.

2.4. Procedure for multiple contaminant systems

Bagajewicz et al. (1999) developed a constructive procedure to solve multiple contaminant systems with centralized or *end of pipe* treatment scheme. This procedure is based on a combinatorial search where all possible maximum reuse structures of the system are analyzed in a tree-type fashion using a branch and bound strategy. In this procedure, a maximum reuse structure is defined as a reuse sequence in which the flow pattern of connections of each process is given by maximum wastewater reuse, or equivalently, by minimizing freshwater consumption of each process that is individually analyzed. This is accomplished by the following linear programming problem:

$$\left.\begin{array}{l} \mathrm{P5}=\min F_j^w \\ \text{s.t.} \\ \sum_i F_{i,j}(C_{i,s,\mathrm{out}}-C_{j,s,\mathrm{in}}^{\max})-F_j^w C_{j,s,\mathrm{in}}^{\max}\leqslant 0 \quad \forall j\in N,\forall s \\ \sum_i F_{i,j}(C_{i,s,\mathrm{out}}-C_{j,s,\mathrm{out}}^{\max})-F_j^w C_{j,s,\mathrm{out}}^{\max}+L_{j,s}\leqslant 0 \quad \forall j\in N,\forall s \\ F_{i,j}\leqslant F_i \quad \forall i,j\in N \end{array}\right\} \tag{5}$$

Thus, the processes are arranged in different sequences, and problem P5 is solved for each process in the sequence using as data the wastewater flows and concentrations of the previously solved processes. This procedure was extended to distributed treatment systems with one decentralized treatment by Bagajewicz and Rivas (2000). The same tree-searching methodology is used, including processes as well as decentralized treatment units as nodes of each reuse sequence. The evaluation of each reuse structure involves two main steps: First, the flow pattern of connections of all upstream processes of the decentralized treatment units are determined by applying, node by node, the maximum reuse rule (P5) and cutting criteria as they were developed by Bagajewicz et al. (1999). The second step requires the development of an iterative algorithm for determining the flow pattern of connections of all downstream processes of the decentralized treatment units. We modified the maximum reuse rule for each downstream process presented by Bagajewicz and Rivas (2000) to include more than one decentralized treatment into the reuse structure. The new version is:

$$\left.\begin{array}{ll} \mathrm{P6}=\min F_j^w & \\ \text{s.t.} & \\ \sum_{k=1}^{T} F_{t_k,j}(C_{t_k,s,\mathrm{out}}-C_{j,s,\mathrm{in}}^{\max})+\sum_{i=1}^{j-1} F_{i,j}(C_{i,s,\mathrm{out}}-C_{j,s,\mathrm{in}}^{\max})-F_j^w C_{j,s,\mathrm{in}}^{\max}\leqslant 0 & \forall j,\forall s \\ \sum_{k=1}^{T} F_{t_k,j}(C_{t_k,s,\mathrm{out}}-C_{j,s,\mathrm{out}}^{\max})+\sum_{i} F_{i,j}(C_{i,s,\mathrm{out}}-C_{j,s,\mathrm{out}}^{\max})-F_j^w C_{j,s,\mathrm{out}}^{\max}+L_{j,s}\leqslant 0 & \forall j,\forall s \\ F_{t_k,j}=\sum_{i=1}^{j} F_{i,t_k}^{j}-\sum_{i=1}^{T} F_{t_k,t_i}^{j} & \forall k\in T \\ F_{i,j}+\sum_{k=1}^{T} F_{i,t_k}^{j}\leqslant F_i-\sum_{k=j+1}^{j-1} F_{i,k}-\sum_{k=1}^{T}\sum_{p=m+1}^{j-1} F_{i,t_k}^{p} & \forall i,j \\ \sum_{k=1}^{T} F_{j,t_k}\leqslant F_j^w+\sum_{i=1}^{j-1} F_{i,j}+\sum_{k=1}^{T} F_{t_k,j} & \end{array}\right\} \tag{6}$$

When decentralized treatment units are included in the reuse structure, the flows between the processes, between the treatment units and the processes, and from one treatment unit to another have to be considered in this modified model. In the above formulation, the concentration of water from a treatment unit ($C_{t_k,s,\mathrm{out}}$) is fixed at the minimum concentration possible for those components that are treated; for other components, concentrations are fixed to an assumed value, which is updated throughout the iterations. The algorithm carries out the iterations until the assumed and calculated concentrations for the water from the treatment for all

Table 1
Data for Case #1

Process	Load (g/h)	$C_{\mathrm{in}}^{\max}$ (ppm)	$C_{\mathrm{out}}^{\max}$ (ppm)
(1) Washing I	626.22	5.00	76.00
(2) Washing II	0.6174	0.00	0.07
(3) Scrubber I	1152.14	30.00	411.00
(4) Scrubber II	246.24	30.00	144.00
(5) Flare seal pot	163.35	100.00	281.50

Table 2
Data for treatment

Treatment type	$C_{t,\mathrm{out}}^{\min}$ (ppm)	a'_R (\$/kg of cresol)
(6) Oil	40	116.6
(7) Light gas	3	434.7

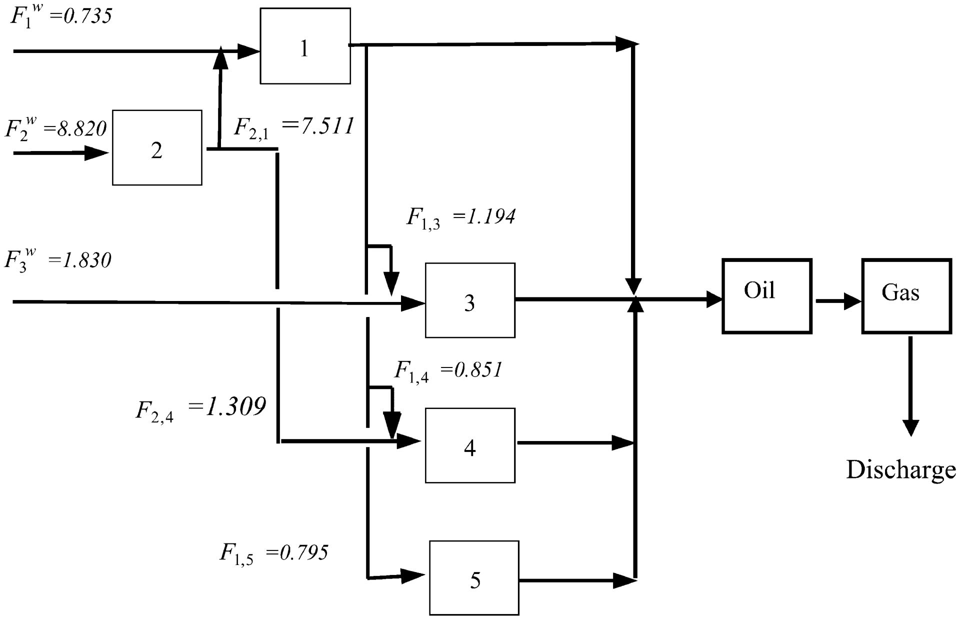

Fig. 1. Tricresyl phosphate solution network with reuse and *end of pipe* treatment.

non-treated components converge, such that:

$$C_{t_k,s,\text{out}} = C^{\text{Assum}}_{t_k,s,\text{out}} \approx \frac{\sum_{j=1}^{N}\left(\sum_{i=1}^{j} F^j_{i,t_k} C_{i,s,\text{out}} + \sum_{i=1}^{T} F^j_{t_i,t_k} C_{t_i,s,\text{out}}\right)}{\sum_{j=1}^{N}\left(\sum_{i=1}^{j} F^j_{i,t_k} + \sum_{i=1}^{T} F^j_{t_i,t_k}\right)} \qquad (7)$$

Complete details of this methodology are given elsewhere (Koppol and Bagajewicz, 2002). We concentrate in this paper in the applications.

3. Case studies

Using the models discussed above, four industrial cases are optimized without the addition of treatment

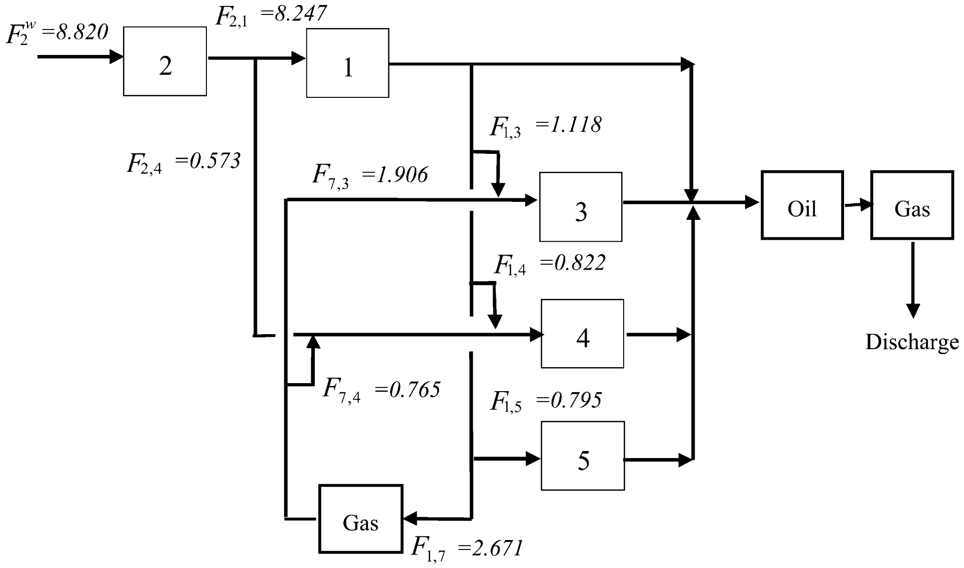

Fig. 2. Tricresyl phosphate solution network with gas regeneration.

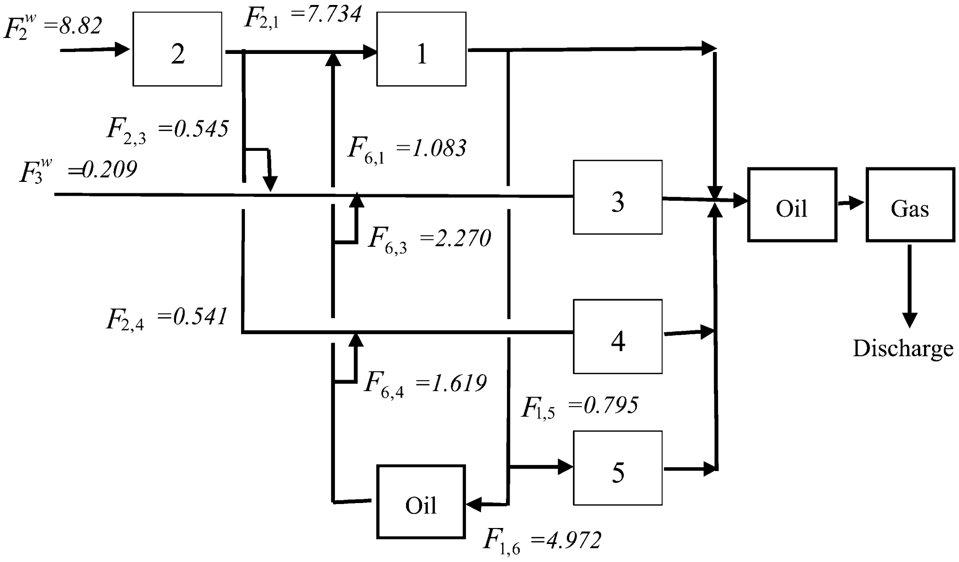

Fig. 3. Tricresyl phosphate solution network with oil regeneration.

units and then compared to the effect of adding treatment units. Different *end of pipe* and regeneration configurations are analyzed in each case to determine the minimum liquid discharge possible and the total operating cost required to achieve it. Furthermore, the effect of varying the regeneration concentration on the amount of freshwater consumed, the amount of wastewater regenerated, and the total costs are discussed. The industrial cases studied are: a tricresyl phosphate process and an ethyl chloride process (taken from El-Halwagi, 1997), a paper mill process (Tripathi, 1996; Brezniak, 1999; Smook, 1994), and a petroleum refinery.

3.1. Case #1: tricresyl phosphate plant

Tricresyl phosphate is a flame retardant produced from cresols mixed with phenol and xylenols. The flame retardant is commonly used in flexible PVC, cellulose nitrate, ethylcellulose coatings, and various rubbers. Tricresyl phosphate is being purified in the process to remove the unreacted raw material, cresol. The process incorporates two washers for product purification, two scrubbers and a flare seal pot for the removal of the contaminant from the off-gas. Table 1 presents the allowable feed and effluent cresol concentration for

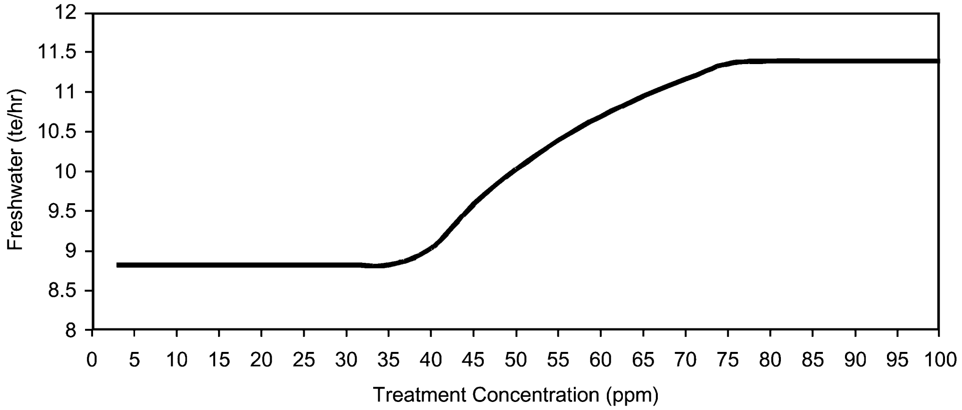

Fig. 4. Freshwater reduction by addition of treatment process.

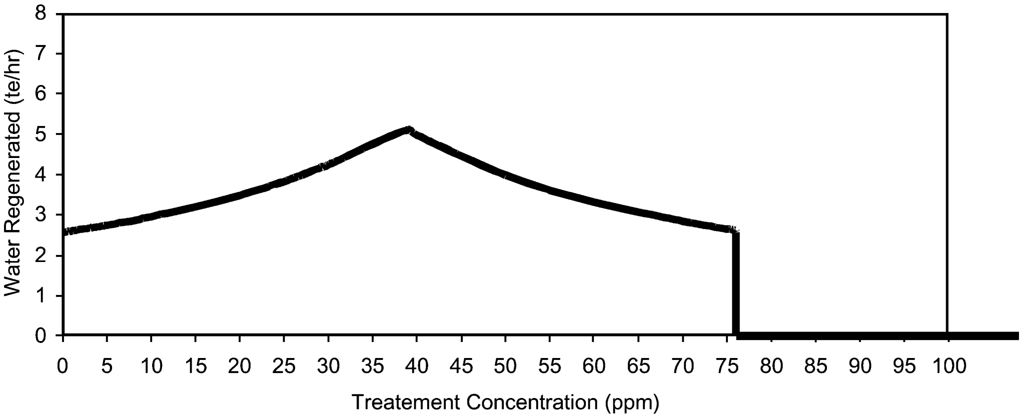

Fig. 5. Water regenerated by addition of treatment process.

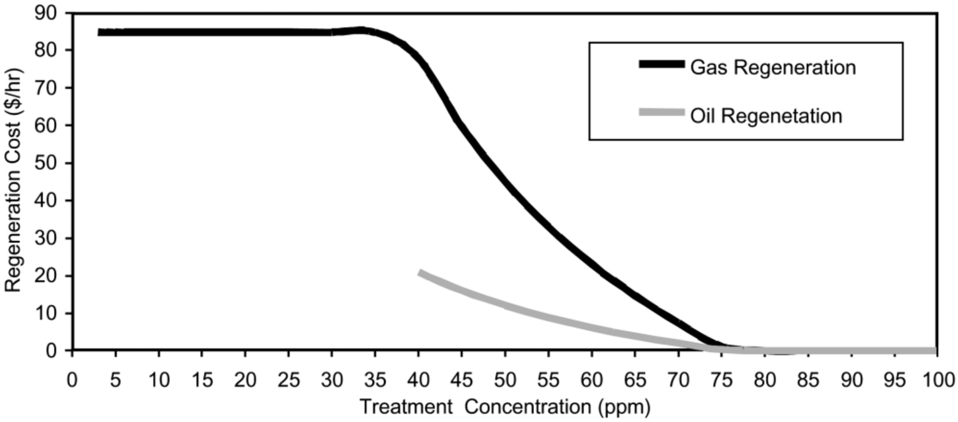

Fig. 6. Regeneration cost vs. concentration.

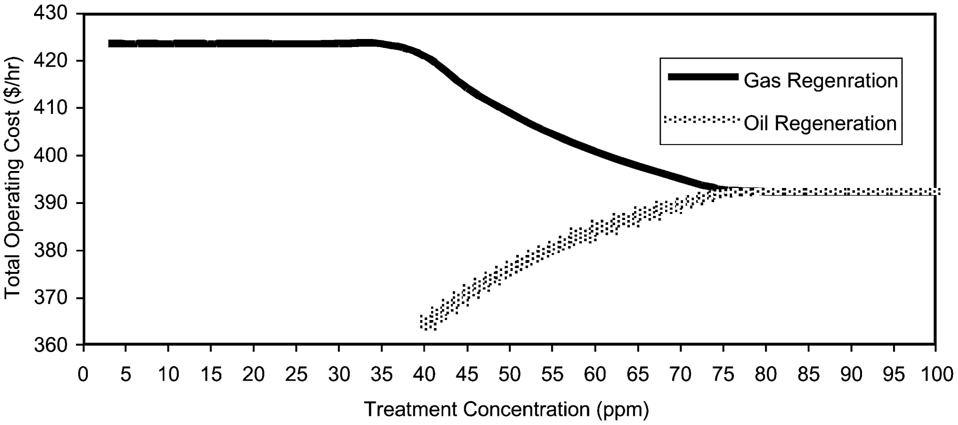

Fig. 7. Total operating cost by addition of a treatment.

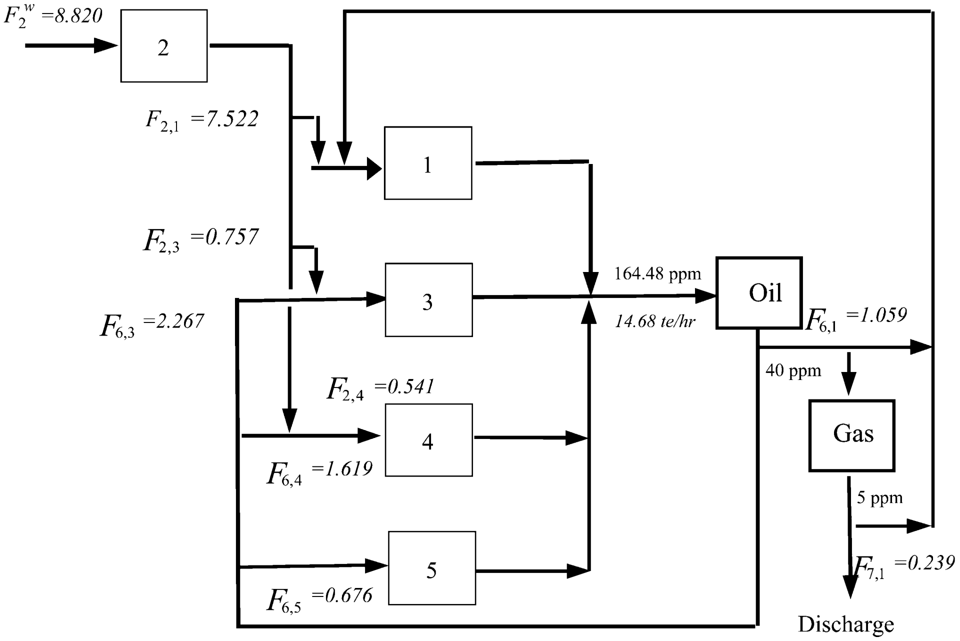

Fig. 8. Tricresyl phosphate solution network with reuse and distributed treatment.

each process, and the contaminant load permitted. Light gas or oil treatment may be used for regeneration. Minimum treatment unit outlet concentrations and costs are shown in Table 2 (El-Halwagi, 1997). The same treatment units, shown in, Table 2 are used for *end of pipe* treatment before discharge. The discharge limit for cresol concentration in wastewater is 5 ppm. Since oil treatment can only clean up to a minimum of 40 ppm, water must be further treated using light gas treatment to meet the discharge limits. Although the light gas treatment can clean up to a minimum of 3 ppm, water is cleaned only to 5 ppm when this treatment is used as *end of pipe* treatment, thus reducing the operating cost. The cost of freshwater and its discharge is 1.5 $/ton.

The minimum freshwater required without reuse and with *end of pipe* treatment for the above data is 22.153 ton/h. The operating cost, including freshwater and *end of pipe* treatment cost, for this case is $4.386 million/yr. The *end of pipe* treatment is oil treatment followed by light gas treatment.

The optimized system, obtained solving P1, where water is reused and the *end of pipe* treatment scheme is employed, is shown in Fig. 1. This optimized network results in saving 10.8 ton/h of freshwater compared to the network without reuse (48% freshwater savings). The cost of freshwater and wastewater treatments is reduced to $3.296 million/yr.

The inclusion of a regeneration step in the network, shown in Fig. 1, further reduces the freshwater consumption. The minimum freshwater consumption that can be achieved using light gas and oil treatments for regeneration are 8.82 and 9.029 ton/h, respectively. The outlet concentration for the water from the regeneration unit is maintained at the lowest possible value, i.e. 3 and 40 ppm for light gas and oil treatments, respectively. The operating cost, which includes freshwater, regener-

Table 3
Alternatives for tricresyl phosphate plant

Water usage scheme	Liquid discharge (ton/h)	Operating cost (million $/yr)
No reuse and no regeneration	22.153	4.386
With reuse and no regeneration	10.8	3.296
Reuse and additional gas regeneration	8.82	3.557
Reuse and additional oil regeneration	9.029	3.057
Reuse and *end of pipe* regeneration	8.82	3.059

Table 4
Data for Case #2

Process	Load (kg/h)	$C_{\text{in}}^{\text{max}}$ (ppm)	$C_{\text{out}}^{\text{max}}$ (ppm)
(1) Reactor I	0.00	0	0
(2) Reactor II	−27.00	65	7
(3) Scrubber I	29.16	8	98
(4) Scrubber II	2.75	0	7

Table 5
Data for Case #2

Treatment type	$C_{\text{in}}^{\text{max}}$ (ppm)	Cost ($/kg)
(5) Air	10	5000
(6) Zeolite	2	58 333

ation and *end of pipe* treatment costs, is $3.557 and 3.057 million/yr with light gas and oil treatments, respectively. The network obtained using light gas and oil treatments as regeneration are shown in Figs. 2 and 3, respectively.

Notice that the operating cost for the network in Fig. 2 is $0.261 million/yr higher than that of the network of Fig. 1. However, the freshwater consumption declines from 11.385 to 8.82 ton/h. Since Process 2 has a maximum inlet concentration of zero, this is the absolute minimum freshwater consumption (unless a new treatment is brought in that produces freshwater). On the other hand, when oil treatment is used for regeneration (Fig. 3) a saving of $0.239 million/yr in the operating cost compared to the network in Fig. 1 is achieved. However the freshwater consumption is not the minimum possible value (8.82 ton/h).

We also investigated the effect of varying the outlet concentration of the treatment unit. The resulting variation of freshwater consumption and the amount of water regenerated vs. the concentration of the regenerated water is shown in Figs. 4 and 5.

At high regeneration, concentration the freshwater consumption is 11.385 ton/h, which is same as the freshwater requirement without the regeneration process in the network (Fig. 1). Regeneration is not necessary if the water cannot be treated to a concentration below 76 ppm, which is the maximum inlet concentration of Process 1. Thus, there is no need for treatment. The flow rate through the regeneration unit goes through a maximum. However, this maximum does not occur when the cost is analyzed. When water is treated to concentration below 76 ppm, regenerated water is used in Washing I. Between 76 and 38 ppm, the amount of water regenerated steadily increases because of the increasing requirement of low concentration water. At the same time the freshwater consumption also steadily decreases, as regenerated water is used instead of freshwater. At approximately 38 ppm concentration of regenerated water the system requires 8.82 ton/h of freshwater, which is the water sent to a freshwater consuming process (Washing II). Therefore, although the regenerated water concentration can be reduced to below 38 ppm this does not reduce the freshwater consumption. On the other hand, with the availability of regenerated water with a concentration lower than 38 ppm, the amount of water regenerated steadily decreases, because it has higher quality.

Figs. 6 and 7 show the regeneration and the total operating cost variation with the concentration of regenerated water for gas and oil treatment. At concentrations above 76 ppm no regenerated water is used, so the total operating cost will be the sum of freshwater cost and *end of pipe* treatment cost. As the concentration of regenerated water decreases the freshwater requirement decreases and the load removed in the regenerating

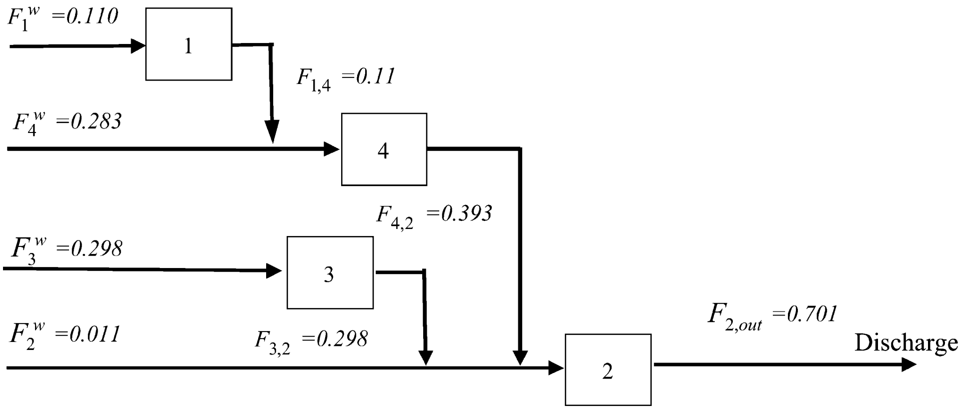

Fig. 9. Ethyl chloride network with reuse and without regeneration.

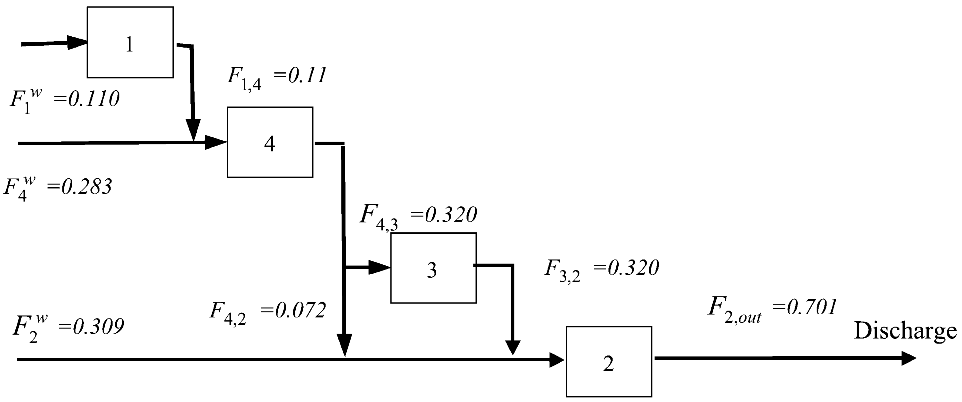

Fig. 10. Ethyl chloride network with reuse and without regeneration.

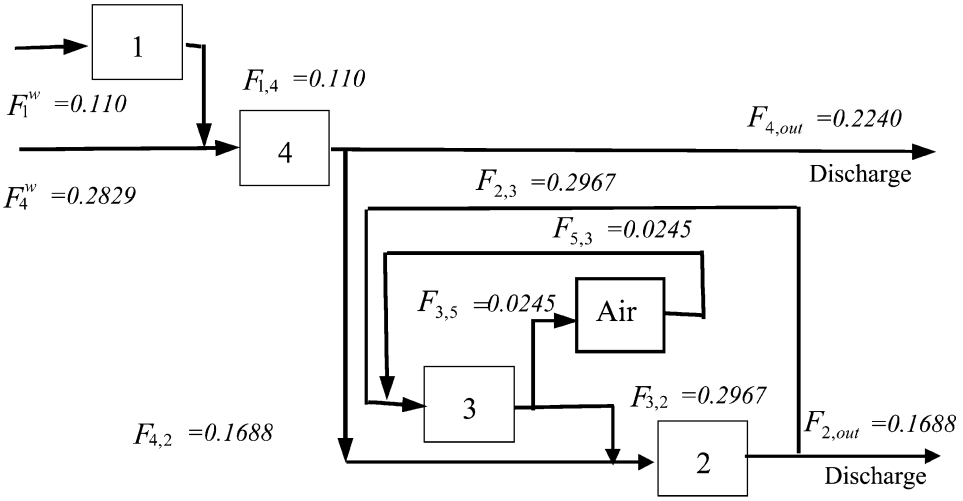

Fig. 11. Ethyl chloride network with reuse and regeneration.

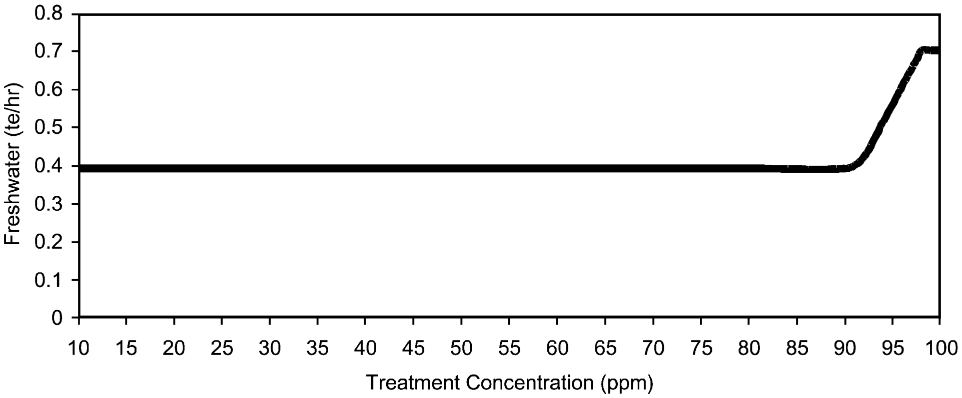

Fig. 12. Freshwater requirement by addition of air treatment.

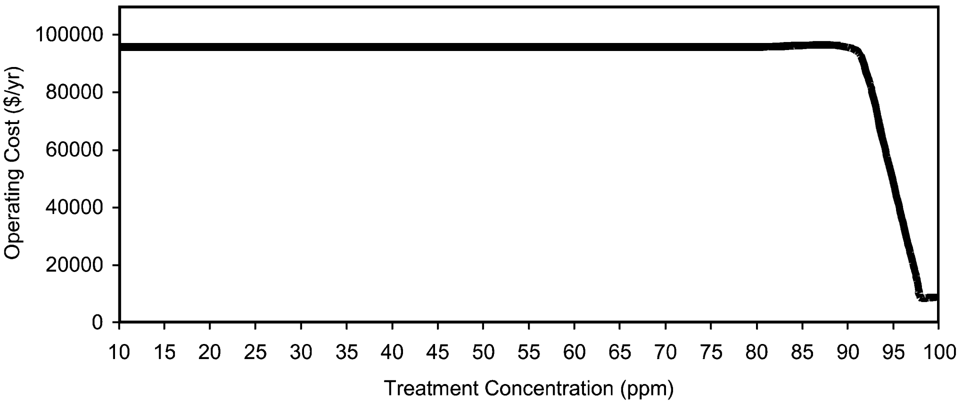

Fig. 13. Total operating cost by addition of air treatment.

processes increases until the outlet concentration reaches 38 ppm. Therefore, the regeneration cost, for gas and oil regeneration, increases with the decrease in concentration of regenerated water in the interval 38–76 ppm. The total operating cost in this interval behaves differently for gas and oil regeneration. From Fig. 7 one can infer that using oil treatment is profitable, while using gas treatment is not profitable. This is because the increase in regeneration cost is smaller than the decrease in freshwater and *end of pipe* treatment cost, while this is not the case when gas regeneration is used, because gas regeneration is nearly three times more expensive than oil regeneration. For the concentration interval below 38 ppm, where the freshwater consumption remains unchanged, the load removed in the regeneration processes is also constant. Therefore, the regeneration cost and total operating cost do not change either.

In situations like this, where the *end of pipe* treatment and regeneration consist of the same treatment technologies one might consider using the water from *end of pipe* treatment directly rather than using separate intermediate regeneration units. This option is also explored for the tricresyl phosphate plant and it is found that this option costs nearly as much as regeneration with oil treatment but ensures the minimum freshwater consumption possible. Fig. 8 shows the network that uses water from *end of pipe* treatment without intermediate regenerating process.

The minimum freshwater consumption is 8.82 ton/h, which is the requirement of the freshwater consuming

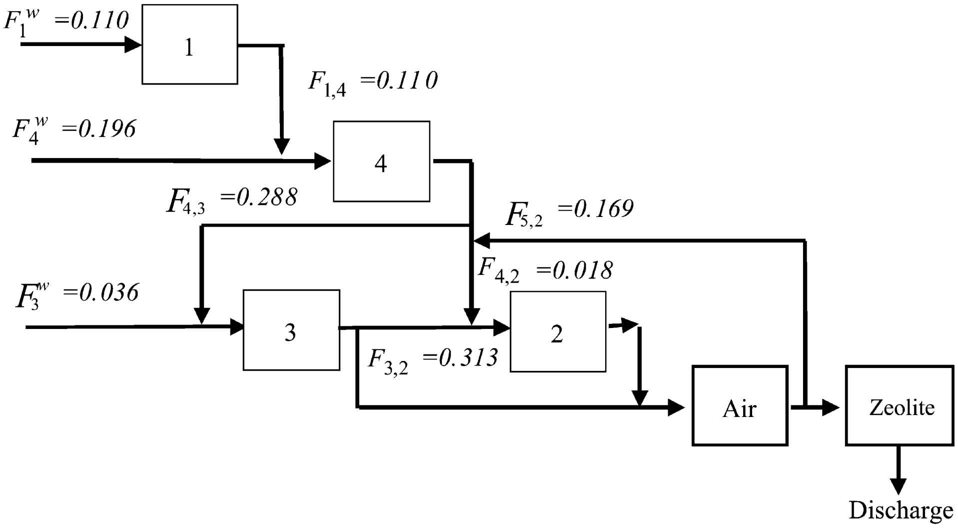

Fig. 14. Ethyl chloride network with air regeneration.

Table 6
Alternatives for ethyl chloride plant

Water usage scheme	Liquid discharge (ton/h)	Operating cost (thousand $/yr)
No reuse and no regeneration	0.701	8.838
Reuse and air regeneration	0.393	95.67
Reuse with air and zeolite regeneration (Larger Scrubber II and Reactor II outlet concentration)	0.342	652.7

process (Washing II). When the concentration of water from oil and light gas treatment are 40 and 5 ppm, respectively, the operating cost is $3.059 million/yr. Notice that the cost of using oil as regeneration (with 40 ppm as the outlet concentration) and *end of pipe* treatment, that is, for the network shown in Fig. 3 the operating cost is $3.057 million/yr but the freshwater requirement for this network is 9.029 ton/h. The additional cost for the network of Fig. 8 is explained because more water is treated in gas treatment, which is a part of *end of pipe* treatment, compared to the network in Fig. 3. The freshwater consumption using the scheme shown in Fig. 8 cannot be reduced below 8.82 ton/h even though the concentration of water from light gas treatment can be reduced to 3 ppm, as one of the processes (Washing II) can use only freshwater ($C_{\text{in}}^{\max}=0$ ppm) and is the only process that is consuming freshwater. We summarize our findings in Table 3.

Thus, zero liquid discharge is not possible in this case. The minimum liquid discharge that is possible with the available treatment technologies is 8.82 ton/h, with an operating cost of $3.059 million/yr (Fig. 8). Nevertheless, these values are remarkably smaller than the discharge of 22.153 ton/h and an operating cost of $4.386 million/yr, which are achieved in the network without reuse and regeneration.

3.2. Case #2: ethyl chloride process

Ethyl chloride was originally produced in the manufacture of tetraethyl lead, an antiknock additive in engine fuel, but today it also serves as an ethylating agent, solvent, refrigerant, and local and general anesthetic. Catalytically reacting ethanol and hydrochloric acid produces this colorless, mobile liquid. Here, ethylene is used as raw material to produce ethanol through a catalytic hydration process in Reactor I. In this process, no contaminant is produced so the water may be reused. The ethanol is then sent to Reactor II where it is reacted with hydrochloric acid to produce ethyl chloride. The effluent from Reactor II is sent through two scrubbers to remove the contaminant of our focus, chloroethanol, which is a by-product formed in Reactor II. The limiting inlet and outlet concentrations and contaminant loads (El-Halwagi, 1997) are shown in Table 4. El-Halwagi (1997) obtained a solution to this problem using a bilinear formulation. The effluent concentration of Reactor II, in this case study, is fixed to the discharge limit (7 ppm). If necessary the problem can be solved repeatedly with this concentration as a parameter. One can use air or zeolite treatment as a regeneration step for removing chloroethanol. The minimum treatment concentration and cost are shown in Table 5 (El-Halwagi, 1997). The cost of freshwater and its discharge is 1.5 $/ton.

Figs. 9 and 10 show alternative networks with reuse and without regeneration, obtained using model P1. These networks require 0.701 ton/h of freshwater. The operating cost is 8838 $/yr. Note that Reactor II requires freshwater even though it is a regenerative process, because this has the purpose of dilution before discharge. The solution presented does not require *end of pipe* treatment as the discharge limits are met for the outgoing water.

The freshwater consumption of the ethyl chloride process can be further reduced from 0.701 ton/h (Figs. 9 and 10) by including treatment in the network. This, however, will increase the operating cost, which is the price to pay if the goal is to reduce the freshwater consumption. The network with inclusion of air treatment with the outlet concentration at 10 ppm is shown in Fig. 11.

The freshwater consumption for the network in Fig. 11 is 0.393 ton/h, and the operating cost is 95 670 $/yr. Notice, in Fig. 5, that the processes that require freshwater are those that can use only freshwater ($C_{\text{in}}^{\max}=0$ ppm). Therefore, no further reduction of freshwater consumption below 0.393 ton/h is possible. This implies that one can use zeolite treatment, which can clean up to 2 ppm, but no further reduction of

Table 7
Data for Case #3

Process	Load (kg/h)	$C_{\text{in}}^{\max}$ (ppm)	$C_{\text{out}}^{\max}$ (ppm)
(1) Pulping/dilution	24 800	500	5000
(4) Deckle showers	21.67	100	500
(5) Cylinder showers	37.50	300	600
(6) Felt showers	3.33	20	100

Table 8
Data for Case #3

Process	Load (kg/h)	$C_{\text{in}}^{\max}$ (ppm)	$C_{\text{out}}^{\max}$ (ppm)
(2) Paper machine (rich)	−18 225	5000	500
(3) Paper machine (lean)	−6480	5000	200

Table 9
Data for Case #3

Treatment type	$C_{t,\text{out}}^{\min}$ (ppm)	Cost ($/ton)
(7) Physical	30	0.15
(8) Physical and membrane	2	0.9

freshwater consumption can be achieved.Figs. 12 and 13 depict the dependency of freshwater requirement and operating cost on the outlet concentration of air treatment.

The system does not require any treated water above 98 ppm, which is the maximum outlet concentration of Scrubber I (3). Therefore, the freshwater requirement and the operating cost when the concentration of treated water is above 98 ppm is the same as that of the network without treatment, which are 0.701 ton/h and 8838 $/yr, respectively. The freshwater requirement steadily drops to 0.393 ton/h as the concentration decreases from 98 to approximately 90 ppm. In this interval, as load removed in treatment also increases, the operating cost increases to 95 670 $/yr. The freshwater consumption remains unchanged as the treatment concentration decreases from 90 to 10 ppm, which is the minimum concentration of air treatment because it has already met its absolute possible minimum. The operating cost does not change in this interval either as the load removed remains constant.

Using higher outlet concentrations for Scrubber II and Reactor II leads to higher operating cost. Indeed Dericks et al. (2001) used 9 and 15 ppm, respectively. The solution for this case is shown in Fig. 14, where Air treatment is used for regeneration and final treatment.

The freshwater consumption and the operating cost for the network of Fig. 14 are 0.342 ton/h and $0.6527 million/yr. A solution by recycling water from *end of pipe* directly is possible, but it requires using zeolite treatment and is too costly. Zero water discharge is not possible in this case because the Scrubber II and Reactor I require freshwater ($C_{\text{in}}^{\max}=0$). Under these circumstances it will be appropriate to minimize the operating cost while meeting the discharge limits, rather than minimizing freshwater. We summarize the results obtained in Table 6.

Thus, zero liquid discharge is not possible in this case either. The minimum liquid discharge possible in this case is 0.393 ton/h, with an operating cost of 95 670 $/yr (Fig. 11). It corresponds to the case where the effluent concentration from Reactor II and Scrubber II are fixed at the discharge limit, i.e. 7 ppm. Notice that this minimum discharge is significantly less compared to 0.701 ton/h, which was the discharge in the network without reuse and regeneration. However, the operating cost in this case is much lower (8838 $/yr). Nonetheless, the liquid discharge can be further reduced to 0.342 ton/h by fixing the effluent concentration from

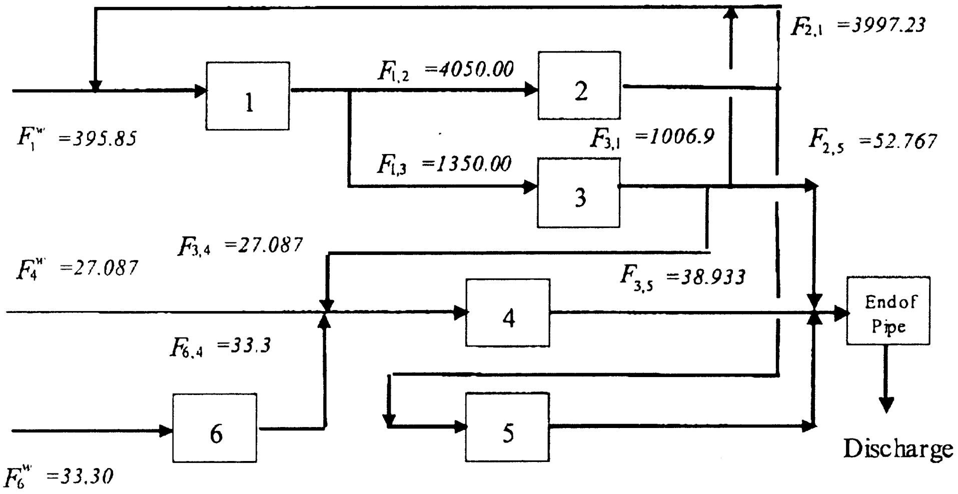

Fig. 15. Paper mill network with reuse and without regeneration.

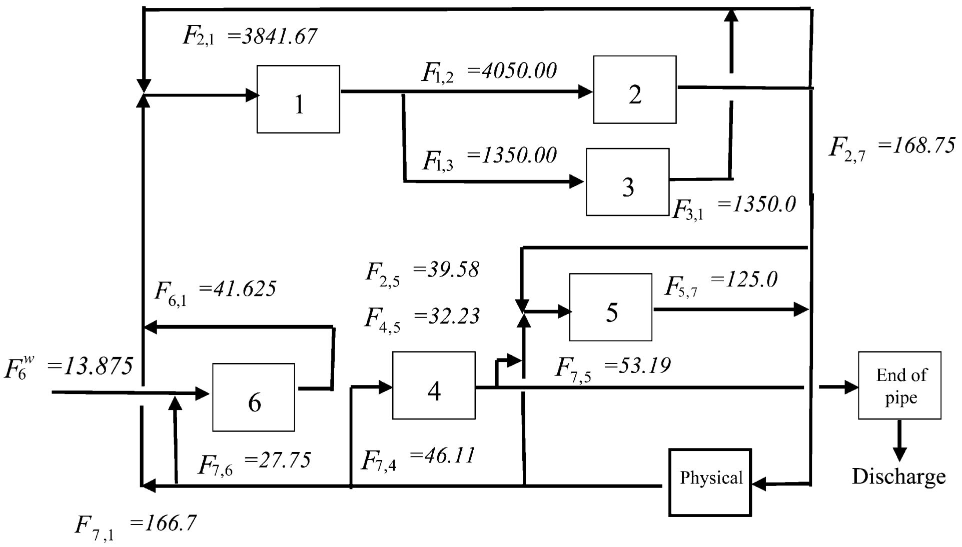

Fig. 16. Paper mill network with physical treatment as regeneration.

Scrubber II and Reactor II at 9 and 15 ppm, respectively. This makes the use of expensive zeolite treatment necessary to meet the discharge limits, raising the operating cost to $0.6527 million/yr.

3.3. Case #3: paper mill

In this case study we will show that paper mills are capable of achieving zero liquid discharge. A 600 ton/day non-bleach paperboard mill is modeled and optimized. The mill consists of chests for pulping and diluting paper fibers, paper machines, showers, and added treatments. In the pulping and dilution steps, there is an addition of contaminant (paper fibers), which is measured as total suspended solids. In the paper machine, the paper fibers are removed and whitewater streams of two different concentrations exit the process. In this case, one should consider the paper machine as

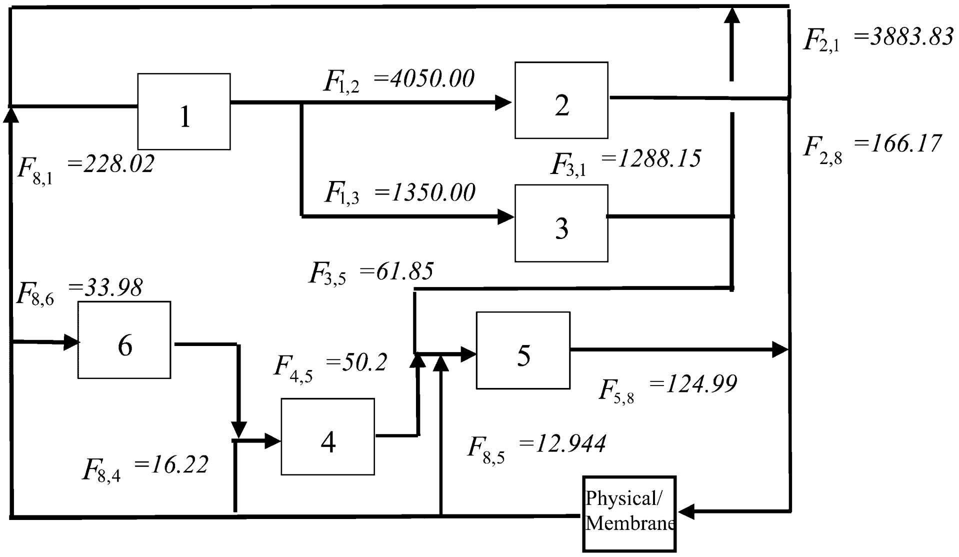

Fig. 17. Paper mill network with membrane/physical regeneration.

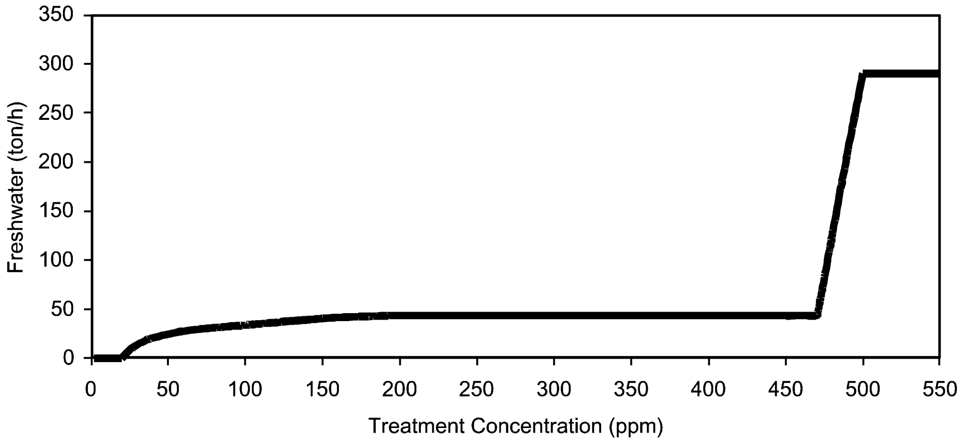

Fig. 18. Freshwater reduction by addition of a regeneration process.

two processes (rich and lean), which have been modeled as additional regeneration processes within the paper mill. The rich white-water is the high-suspended solid wastewater falling from the beginning of the paper machine into a silo. The lean white-water is the low-suspended solid wastewater from the suction boxes. The showers remove paper fibers from the machine itself at different stages. Tables 7 and 8 show the paper mill data including inlet and outlet concentrations and load on process.

The treatments of concern are physical (dissolved air flotation) and a combination of physical and membrane treatment (ultrafiltration), which remove suspended solids from the effluent. The cost and minimum outlet concentration information is shown in Table 9 (Wiseman and Ogden, 1996).

The cost for freshwater and its final treatment, which is a sequence of physical and biological treatment is 1.65 $/ton of water (Wiseman and Ogden, 1996; Lagasé et al., 1998). The cost of final treatment for the water discharged through the regeneration process is 0.35 $/ton. Additional constraints were included in P2, P3 and P4 to prevent paper fiber loss to the waste. These constraints are: (a) all the water from pulping/dilution process is used in the paper machines (rich and lean); and (b) no wastewater is allowed from the paper machine (rich).

It is an almost universal practice for paper mills to reuse the water; thus recovering the valuable paper fiber from excess water sent to paper machines. Fig. 15 shows the optimized network of the original process without treatments, but allowing reuse. The freshwater

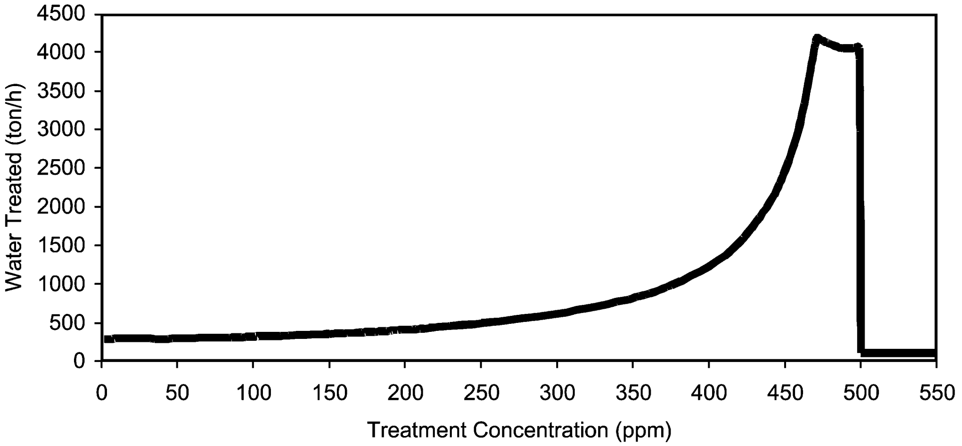

Fig. 19. Amount of water regenerated vs. concentration.

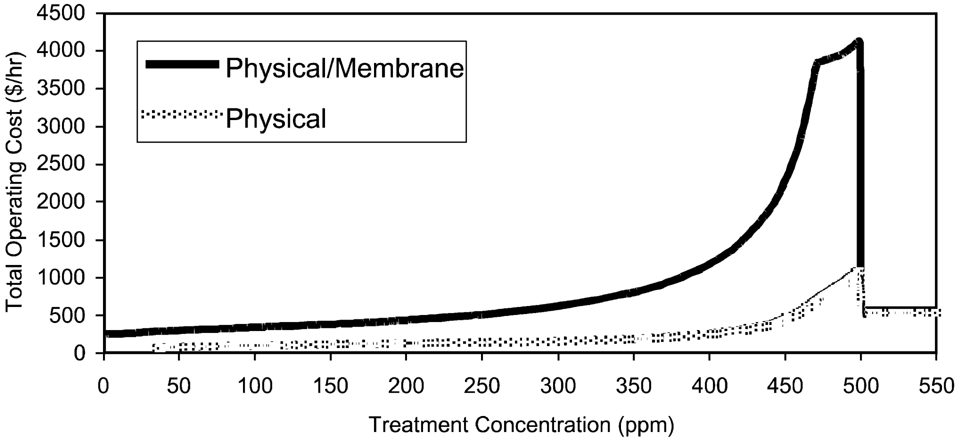

Fig. 20. Total operating cost vs. regeneration concentration.

requirement after reuse is reduced to 456.24 ton/h and much of the white-water is reused. The operating cost for the network of Fig. 15 is $6.32 million/yr, based on 350 operating days/yr. This solution is close to the way many paper mills currently handle their water.

The addition of a physical treatment process for regeneration of used water further reduces the freshwater requirement. This practice is observed in Paper mills. The optimal network using physical treatment as the regeneration step is shown in Fig. 16. The freshwater consumption reduces to 13.875 ton/h, which saves $5.76 million/yr in operating cost compared to the network without regeneration. The resulting operating cost is $0.56 million/yr.

A zero liquid discharge network, obtained by adding a membrane treatment consisting of ultrafiltration and/or reverse osmosis (RO) to the physical treatment as regeneration process is shown in Fig. 17. The resulting operating cost for the zero discharge system is $2.2 million/yr, which is higher than the one shown in Fig. 16. Thus, this is the price to pay if effluent release is an issue.

The effect of concentration of treated water on the amount of freshwater required and the operating cost has also been studied. Figs. 18–20 depict the variation of freshwater consumption, the amount of water treated and the total operating cost as a function of concentration of regenerated water, respectively. In Fig. 18, a zero discharge system is possible when the concentration of treated water is below 20 ppm.

When the concentration of regenerated water is high (above 500 ppm), the freshwater consumption is 290 ton/h, which is not the same as the amount of freshwater required for the network without treatment (456 ton/h). Also, the amount of water treated at a concentration above 500 ppm is not zero (Fig. 19). This indicates that at high treatment outlet concentrations water is sent to treatment resulting in freshwater savings. The constraint that the paper machine (rich) should not discharge water increases the freshwater requirement because the water from paper machine needs to be diluted before reuse to meet the limiting concentration requirement. However, when a physical treatment is used, the water from the paper machine can be discharged after treating, because physical treatment prevents the loss of paper to waste. This obviates the need of additional freshwater required for dilution. Thus, resulting in reduction of freshwater consumption at high treatment concentrations relative to the network in Fig. 15, where water is reused without regeneration.

When the treatment outlet concentration drops below 500 ppm there is a sharp increase in treated water and consequently in costs (Figs. 19 and 20). This is because the water from the paper machine (rich), which has a

Table 10
Alternatives for paper mill

Water usage scheme	Liquid discharge (ton/h)	Operating cost (million $/yr)
Reuse and no regeneration	456.24	6.32
Reuse and physical regeneration	13.875	0.56
Reuse with physical/membrane regeneration	0	2.2

Table 11
Process data for the refinery example

Process	Contaminant	$C_{\text{in}}^{\max}$ (ppm)	$C_{\text{out}}^{\max}$ (ppm)	Load (kg/h)
(1) Caustic treating	Salts	300	500	0.18
	Organics	50	500	1.20
	H_2S	5000	11 000	0.75
	Ammonia	1500	3000	0.10
(2) Distillation	Salts	10	200	3.61
	Organics	1	4000	100
	H_2S	0	500	0.25
	Ammonia	0	1000	0.80
(3) Amine sweetening	Salts	10	1000	0.60
	Organics	1	3500	30.0
	H_2S	0	2000	1.50
	Ammonia	0	3500	1.00
(4) Sweetening (Merox I)	Salts	100	400	2.00
	Organics	200	6000	60.0
	H_2S	50	2000	0.80
	Ammonia	1000	3500	1.00
(5) Hydrotreating	Salts	85	350	3.80
	Organics	200	1800	45.0
	H_2S	300	6500	1.10
	Ammonia	200	1000	2.00
(6) Desalter	Salts	1000	9500	120
	Organics	1000	6500	480
	H_2S	150	450	1.50
	Ammonia	200	400	0.00

concentration of 500 ppm, is treated to reduce its concentration to below 500 ppm before reuse. The freshwater consumption steadily drops to 43.7 ton/h as the concentration of treated water decreases below 500 ppm. The minimum freshwater consumption remains at 43.7 ton/h for the concentration of treated water in the interval 470–200 ppm, but the amount of water treated decreases steadily, thus reducing the operating cost.

Table 12
Treatment data for the refinery example

Process	Contaminant	$C_{\text{out}}^{\max}$ (ppm)	Cost ($/ton)
(7) API separator followed by ACA	Salts	Not treated	0.12[a,b]
	Organics	50	
	H_2S	Not treated	
	Ammonia	Not treated	
(8) RO	Salts	20	0.56[a]
	Organics	Not treated	
	H_2S	Not treated	
	Ammonia	Not treated	
(9) Chevron waste water treatment	Salts	Not treated	1.00[c]
	Organics	Not treated	
	H_2S	5	
	Ammonia	30	

[a] *Source:* Perry and Green (1997).
[b] *Source:* Stenzel (1993).
[c] *Source:* Leonard et al. (1984).

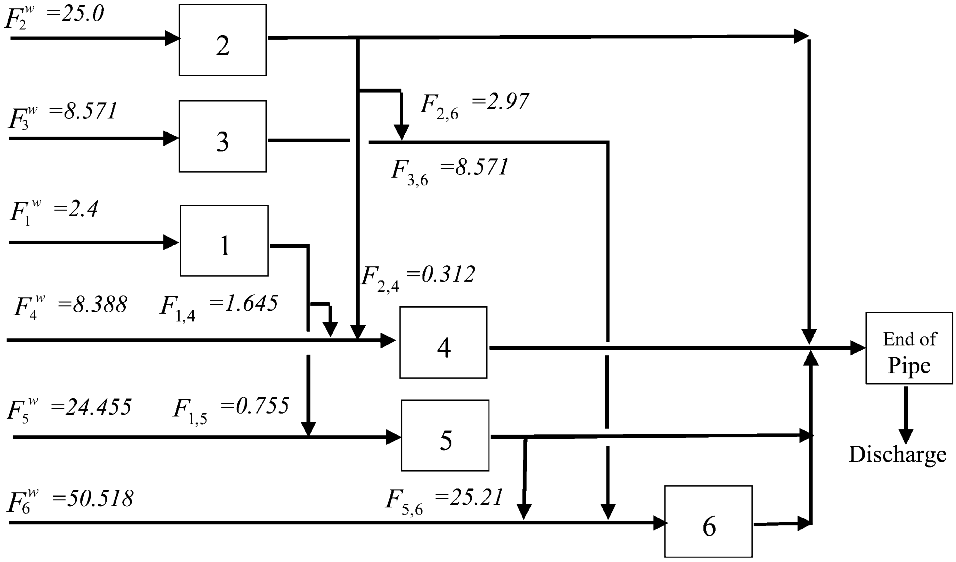

Fig. 21. Refinery network with *end of pipe* treatment.

At concentrations of treated water lower than 200 ppm the freshwater consumption steadily decreases until it is completely eliminated at 20 ppm, as water that is of better quality than the water from paper machine (lean) is available for reuse in this interval. At the same time, the total operating cost of both membrane/physical and physical treatment decreases in this interval, making the zero discharge option profitable. Since zero discharge is attainable when the outlet concentration of treatment falls below 20 ppm, an improvement in the physical treatment may be able to accomplish this, which saves additional operation cost of membrane treatment. All these results are summarized in Table 10.

3.4. Case #4: petroleum refinery

In Petroleum refining, water is primarily used to wash inorganics from hydrocarbons. Along with inorganics, water also accumulates organic contaminants like oil, grease, phenols, cresols, xylenols etc. Some processes use steam as a stripping medium in distillation and as a driving fluid in vacuum ejectors. In this case study, the contaminants in wastewater are broadly classified into four contaminant categories: salts, organics, hydrogen sulfide and ammonia. The sources of wastewater, the load of the contaminants and the limiting inlet and outlet concentration data are shown in Table 11.

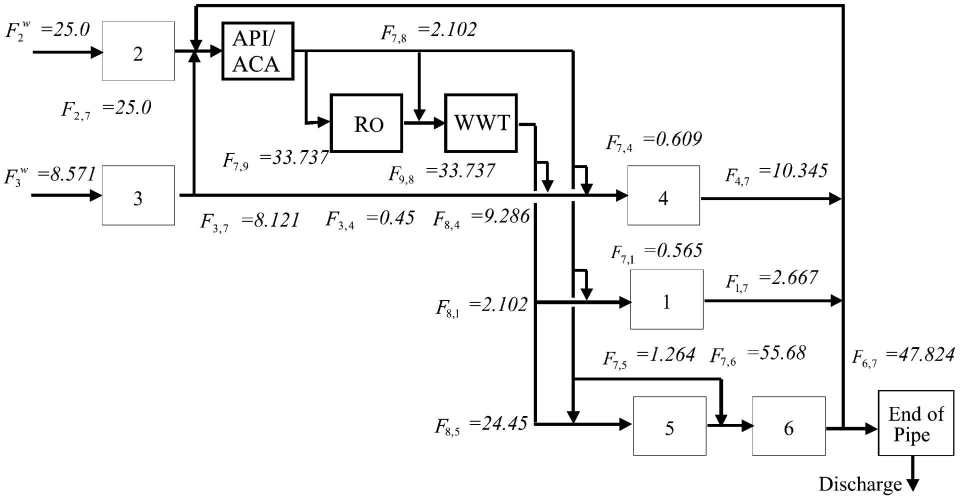

Fig. 22. Refinery network with regeneration.

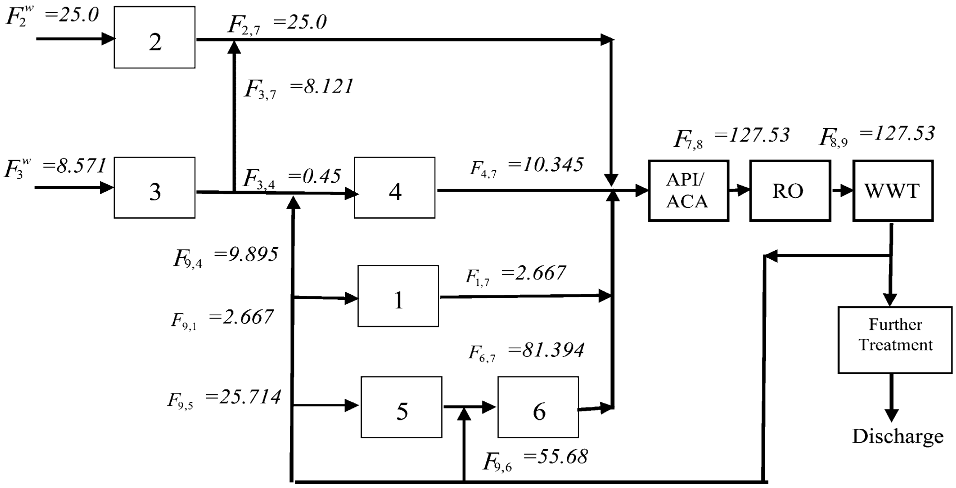

Fig. 23. Refinery network with reuse of *end of pipe* treatments effluents.

The treatment processes that are considered are the API gravity separator, activated carbon adsorption (ACA), RO and the Chevron waste water stripper (WWT). The API gravity separator can remove insoluble organics like oil, grease etc., while ACA can remove soluble organics. However, ACA cannot effectively remove highly soluble organics like alcohols and aldehydes. Because of high concentration level of organics, wastewater needs to be treated in both the API separator and carbon adsorption treatment units before it becomes fit for reuse. The RO treatment can remove salts to an extent that meets discharge limits; the WWT treatment removes hydrogen sulfide and ammonia. The wastewater is treated prior to discharge using biological treatment, which removes the residual organics, and to some extent, the residual ammonia and hydrogen sulfide. The treatment cost and minimum outlet concentration for each contaminant is shown in Table 12. The freshwater and its *end of pipe* treatment cost is 2.00 \$/ton.

Using the data in Table 11, the minimum freshwater required without reuse of the wastewater is 144.8 ton/h, and the operating cost is \$2.43 million/yr. The freshwater requirement is reduced to 119.33 ton/h when the wastewater from the processes is reused and the *end of pipe* treatment scheme is adopted (Fig. 21). The operating cost in this case decreases to \$2.005 million/yr.

When regeneration is considered, the freshwater requirement drops to 33.571 ton/h. The network including the treatments is shown in Fig. 22.

The consumption of the network of Fig. 22 coincides with the total water required by the freshwater of the distillation and amine sweetening processes. The total operating cost, which includes freshwater, treatment and the *end of pipe* treatment costs is \$1.11 million/yr. Therefore, the inclusion of additional treatment units, shown in Table 12, saves \$0.895 million/yr in operating costs.

The other scheme of water supply that one can explore is reusing the effluent of the *end of pipe* treatment. The solution network obtained for this scheme is shown in Fig. 23.

Although the freshwater consumption for the above network is the minimum possible (33.571 ton/h), the operating cost is \$1.889 million/yr. Here, 0.32 \$/ton was the cost for freshwater when biological treatment is used before discharged (denoted as ‘further treatment’ in Fig. 23). Note that this cost is \$0.779 million/yr more compared to the network in Fig. 22. We summarize all the above results in Table 13.

Table 13
Alternatives for refinery

Water usage scheme	Liquid discharge (ton/h)	Operating cost (million \$/yr)
No reuse and no regeneration	144.80	2.430
With reuse and no regeneration	119.33	2.005
With reuse and regeneration	33.571	1.110
Reuse and *end of pipe* regeneration	33.571	1.889

Zero liquid discharge is not possible in this case unless treatment technologies that can completely remove H_2S and Ammonia are available. Nonetheless, when reuse and regeneration are employed, large decreases in liquid discharge (from 144.8 to 33.571 ton/h) and in operating cost (from \$2.43 to 1.11 million/yr), are obtained.

4. Conclusion

In this paper, zero liquid discharge solutions for systems with single and multiple contaminant systems are explored for four industrial cases using the methodologies recently developed. The industrial cases studied are a tricresyl phosphate plant, an ethyl chloride plant, a paper mill and a petroleum refinery. Zero liquid discharge was possible only in the case of the paper mill. Moreover, it was found to be profitable. In the case of tricresyl phosphate plant and petroleum refinery, large reductions in liquid discharge and operating cost are possible by means of reuse and regeneration of wastewater. The study of the ethyl chloride plant showed that significant reduction in liquid discharge could be achieved without use of expensive treatment technologies, like zeolite treatment, and by maintaining the effluent concentrations from the processes below discharge limit. In conclusion, the relationship between the cost of regeneration and the cost of freshwater as well as the discharge concentration of the treatment are the determining factor in the structure and economical feasibility of zero or partial liquid discharge cycles.

Acknowledgments

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Appendix A: Nomenclature

α	targeted freshwater consumption
β	targeted regeneration cost
a_R	cost per unit weight of water flowing through regeneration unit R
a'_R	cost per unit weight of load removed through regeneration unit R
$C_{j,\text{in}}^{\max}$	inlet limiting concentration in process j
$C_{j,\text{out}}^{\max}$	outlet limiting concentration in process j
$\mathrm{C}_{t_k,\text{out}}$	outlet concentration from treatment t_k
$C_{j,s,\text{in}}^{\max}$	inlet limiting concentration for contaminant s in process j
$C_{j,s,\text{out}}^{\max}$	outlet limiting concentration for contaminant s in process j
$C_{j,s,\text{out}}$	outlet concentration for contaminant s in process j
$C_{t_k,\text{s},\text{out}}$	concentration of contaminant s at the outlet of treatment t_k
$C_{t_k,s,\text{out}}^{\text{Assum}}$	assumed concentration of contaminant s at the outlet of treatment t_k
F_j^w	freshwater flowrate to process j
$F_{i,j}$	water flow from process i to process j
$F_{t_k,j}$	water flow from treatment t_k to process j
F_{j,t_k}	water flow from process j to treatment t_k
F_{i,t_k}^j	water flow from process i to treatment t_k while analyzing process j
F_{t_i,t_k}^j	water flow from treatment t_i to treatment t_k while analyzing process j
$F_{j,\text{out}}$	water flowing from process j
F_i	total water flow through process i
i	index representing process i
j	index representing process j
k	index representing treatment process k
L_j	mass load in process j
$L_{j,s}$	mass load of contaminant s in process j
N	total number of processes in the network
p	index representing process p
T	total number of treatment units available in the network
U	upper bound for flows
$Y_{i,j}$	binary variable representing connection between process i and process j
$Y_{w,j}$	binary variable representing freshwater connection to process j
$Y_{j,o}$	binary variable representing outlet connection for process j

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