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A review of recent design procedures for water networks in refineries and process plants☆

Miguel Bagajewicz *

School of Chemical Engineering and Materials Science, University of Oklahoma, 100 E. Boyd St, T-335, Norman, OK 73019, USA

Abstract

This paper presents a review of the procedures to design and retrofit water networks. Although the emphasis is in showing results for refineries, the methods are valid for any process plants. It is first shown that the problem has been decomposed into the design of two interacting subsystems. One problem is the freshwater and wastewater reuse allocation and the other is the wastewater treatment problem. It is also shown how the wastewater treatment problem was modeled as a distributed and decentralized treatment. The roadmap towards zero liquid discharge and energy integrated solutions is then discussed. Several solution approaches are briefly outlined emphasizing the main trend leaning towards the use of mathematical programming. The major claim made is that mathematical programming can produce globally optimal solutions and practically important sub-optimal solutions when conceptual insights are employed to build the models. Although the paper intends to be comprehensive, it emphasizes the author's recent work. Finally, a few of the existing challenges of the area are outlined. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Water systems; Wastewater minimization; Wastewater reuse; Wastewater recycle; Wastewater regeneration; Wastewater treatment

1. Introduction

Water is a key element for the normal functioning of the chemical and petrochemical industry. Steam stripping, liquid–liquid extraction and washing operations are among the many processes present in refineries and chemical plants where water is intensively utilized.

In refineries, steam is used in atmospheric and vacuum crude fractionation, as well as in coking, hydrocracking, FCC, visbreaking, sweetening, hydrotreating, alkylation, ether synthesis, etc. In addition, water is used in desalters to remove primarily the salted water droplets that the crude contains. However, several other contaminants are also removed (H_2S, suspended solids, ammonia, etc). In caustic treating water is used and the principal contaminants are H_2S, ammonia, phenol, mercaptans, etc. Water is also intensively used in hydrometallurgy where many suspended solids as well as a large variety of ionic metals can be found. In addition, since liquid–liquid extraction is often used, organic solids are also present. In the iron and steel industry vast amounts of water are used in cooling of blast furnaces and casting machinery, quenching of slag, scrubbing of gases with waste waters containing sulfides, cyanides, sulfur dioxide, calcium oxide and chromates. The food and agricultural industries (sugar factories, dairy industries, breweries) make use of water for a variety of washing operations and steam in evaporators. Other industries with intense use of water are the textile industry, the pharmaceutical and electronic component industry.

Several measures exist to assess the quality of water for discharge. For example, the total organic carbon (TOC), the biochemical oxygen demand (BOD) and the chemical oxygen demands (COD) indicate the organic matter content. Oil and grease (O&G) and total petroleum hydrocarbons (TPH) give a measure of the presence of oil, grease and other hydrocarbons. The physical characteristics of the wastewater are also adjusted before disposal. These characteristics include the total suspended solids (TSS), pH, temperature, color and odor. In compliance with the United States EPA Clean Water Act of 1977, wastewater must be treated

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* Tel.: + 1-405-3255811; fax: + 1-405-3255813.

E-mail address: bagajewicz@mailhost.ecn.uoknor.edu (M. Bagajewicz).

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before discharge (that is, end of pipe treatment). Several treatment options are taken into account depending on the sludge characterization. In other words: wastewater treatment procedures are based on the type and concentration of its contaminants.

In refineries, treatment is divided in four levels: primary treatment involves physical treatment processes, secondary treatment comprises operations where soluble matter is removed, and tertiary and quaternary treatments 'polish' the effluent to the final discharge standards. In other industries, this classification is sometimes also found. Regardless of the treatment level, the unit operations for wastewater treatment are classified as physical (air flotation, oil coalescing, evaporation, filtration, etc.), chemical (precipitation, coagulation, ion exchange, etc.), thermal, and biological.

Several procedures have been proposed to design economical wastewater treatment. With a few exceptions, these procedures rely on the application of certain rules of thumb. The current installations usually merge several waste streams and use appropriate technologies in series to clean this stream before disposal. These are therefore, end-of-pipe non-distributed wastewater cleanup solutions. Several papers discuss these options. Belhateche (1995) offers a complete discussion of these technologies.

Starting in the eighties and increasingly in the nineties, water re-use started to become popular as a means of reducing the total amount of water intake. This, in turn, not only saves upstream treatment of raw water but also reduces wastewater treatment costs. In addition, the concept of distributing the treatment among the various polluted streams and even decentralizing it is gaining acceptance. Industry and the EPA in the US are also seriously considering and discussing the advantages and disadvantages of zero liquid discharge solutions as the ultimate goal of green water utilization in process plants.

In this paper, the state of the art in water allocation and water treatment process solutions is reviewed. Special emphasis is put to discuss those methods based on mathematical programming, as they are becoming the focus approach that almost all researchers are using to solve these problems. The central claim made in this review is that mathematical programming can efficiently produce globally optimal and sub-optimal solutions if conceptual insights are made to properly build the models.

2. Roadmap for improved process solutions

Until a few years ago, the problem of water treatment was considered as a set of sequential treatment operations of a single wastewater stream consisting of the wastewater from all unit operations (desalters, strippers, etc). At the same time, without the concept of wastewater reuse, these processes are fed by freshwater only. Such a system is depicted for three water user processes (P_i) and three treatment units (T_i) in Fig. 1(a). One way of obtaining improved designs is the reuse of wastewater from one process to feed another without sending it to treatment first. This reduces the cost because the overall water intake is smaller (Fig. 1(b)). The next step is to introduce series/parallel designs of the wastewater treatment unit without merging all the wastewater streams (Fig. 1(c)). Finally, treatment can be decentralized in such a way that some pollutants are removed from wastewater of selected processes allowing the reuse of these waters (Fig. 1(d)).

The concept of zero discharge applies alternatively to the total elimination of the disposal of environmentally hazardous substances or to the concept of a closed circuit of water, such that water disposal is eliminated altogether, that is zero 'liquid' discharge. Closed circuits are appealing because end-of-pipe regeneration

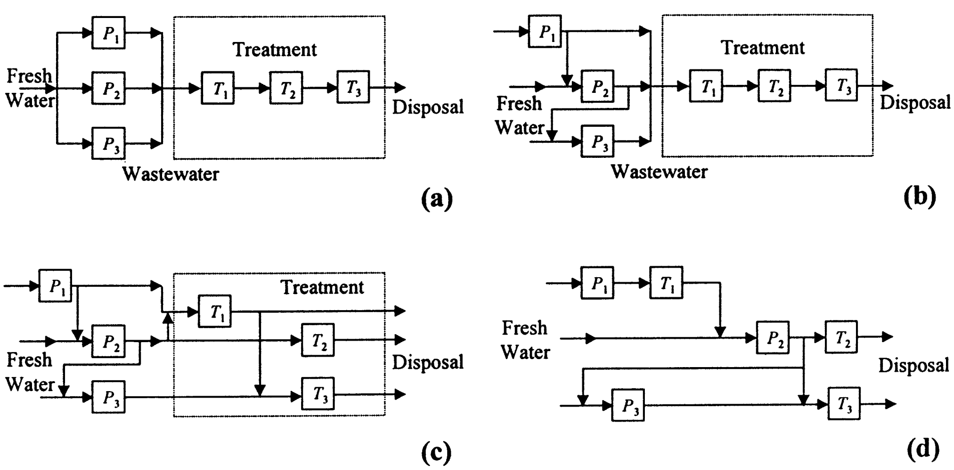

Fig. 1. Water utilization systems in process plants.

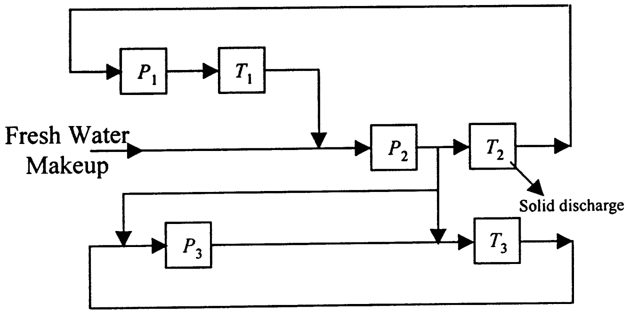

Fig. 2. A zero liquid discharge scheme.

does not have to be conducted to the full extent required for disposal as water can be reused with higher level of contaminants (Fig. (2)). Additionally, the absence of a discharge eliminates internal administrative costs associated with the enforcement of environmental protection agencies and local limits as well as the interface with other government agencies.

These zero discharge process solutions have never been attempted, neither in academic case studies, and apparently nor in practice. They constitute the burning challenge for both academia and industry. There are however, a few issues than can readily be pointed out. First, many units require steam, that is, pure fresh water of boiler quality. Thus, in order for these zero discharge cycles to exist, wastewater cleanup should be thorough, something that could be too expensive to be realistic. Second, unless an expensive total evaporation step is included, some water make-up and disposal should take place to avoid the accumulation of certain species not being removed.

The analysis made in this section suggests that in reality the problem one wishes to solve is the one depicted in Fig. 2, which has all the previous alternatives embedded. Diepolder (1992) and Goldblatt, Eble and Feathers (1993) discussed how realistic is this concept from the practical point of view, addressing issues such as the disposal of solids, the possible sizable revenues obtained for the selling of low grade salts and avoiding their disposal (close to a million dollars per year for a typical refinery), or the costs of disposal of groundwater solids, etc.

To attack the problem at its roots, i.e. the generation of pollutants, process simulation was proposed as a tool to perform pollution balances on processes and calculates pollution indices (Sowa, 1994; Hilaly & Sikdar, 1996). One of the main results of this line of work is the WAR algorithm developed by the US EPA Risk Reduction Engineering Laboratory. However, for many processes the reduction of the generation of pollutants is not possible. The petroleum processing industry is such an example. The major pollutants in refinery wastewater are part of the crude and are not generated in the plant. Many other pollutants are by-products that are difficult to reduce.

There have been traditionally two approaches used to obtain good designs of these systems:

- conceptual approach;
- mathematical programming.

It is interesting to note that the seminal paper of this area (Takama, Kuriyama, Shiroko & Umeda, 1980) proposed a mathematical programming approach to design a structure similar to the one in Fig. 1(d). However, in view of all the implementation limitations and difficulties that the approach used by Takama et al. (1980) presented, the conceptual approach that dominated the field using structures like the one in Fig. 1(a) or (b). However, in the last few years, the conceptual design paradigm is showing limitations to address the complexity of the problem. Despite these limitations, the conceptual approach has provided a simplified description of the problem that has been of great value to build effective mathematical programming models. Recent work is proving that a synergistic combination of both approaches, that is, the use of conceptual insights to help formulating better models for mathematical programming (good initial points, heuristics to help in branch an bound procedures, use of necessary conditions of optimality, etc) is at this point in time showing to be the most effective alternative.

Graphical insights are of importance in practice because they allow the engineer to incorporate many factors that mathematical programming does not consider. Thus, the field has evolved from a paradigm where a graphical insight was used to obtain a design to another where a mathematical is used, from which a graphical representation is obtained.

As it was outlined above, the research community has not addressed the problem of optimizing the structure of Fig. 2 directly. It has instead focused in the solution of either the minimization of freshwater usage through re-use and proper allocation of wastewater, or the series/parallel clean-up structure. That is, it has partitioned the problem of Fig. 1(c) into two sub-problems. We now review the work performed in each of these sub-problems separately.

3. Optimal water/wastewater allocation

The search for optimal wastewater reuse solutions was addressed by industry itself more than 20 years ago (Carnes, Ford & Brady, 1973; Skylov & Stenzel, 1974; Hospondarec & Thompson, 1974; Mishra, Fan & Erickson, 1975; Anderson, 1977; Sane & Atkins, 1977). Takama et al. (1980) used mathematical programming to solve a refinery example. A superstructure of all water-using operations and cleanup processes was set up and an optimization was then carried out to reduce the system structure by removing irrelevant and uneconomical connections. The authors made an important

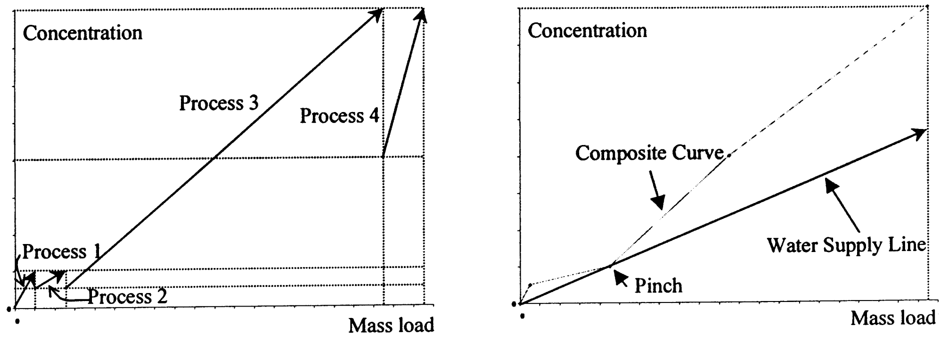

Fig. 3. Targeting procedure for single component systems.

contribution by addressing the problem of water management as a combination of water/wastewater allocation among processes and wastewater distribution to cleanup units. This can be considered as the seminal paper in this area.

Although multiple pollutants are almost always present, sometimes for the purpose of analyzing the reuse of wastewater, pollutants can be lumped in a single pseudo-pollutant or ignored if their concentration is too low. This has prompted a classification on single pollutants and multiple pollutants problems, for which a variety of methods have been developed. It was not until very recently when the issue of energy efficient utilization was researched.

The problem has received a lot of attention form the academic community and from practitioners. At least one book is devoted entirely to the problem (Mann & Liu, 1999) and another discusses it in detail (Rossiter, 1995). In addition, there are a few commercial software companies offering products related to water management. Even though it seems like a separate area of research, the problem is a mass exchange problem. Indeed, contrary to recent claims (Alva-Argáez, Vallianatos & Kokossis, 1999), although some processes are not countercurrent mass exchangers, it can be modeled as a one lean stream (water) and many rich streams (processes) system.

3.1. Conceptual design procedures

The hierarchical design approach (Douglas, 1988), proposes to start with some critical equipment of the flowsheet (usually the reactor) and continue building the flowsheet from the inside out going through the separation system and later through the heat recovery system. As applied to water/wastewater reuse systems the conceptual design approach was initiated by Robin Smith from UMIST, who proposed a targeting procedure that allows the calculation of the minimum fresh water usage without the need of constructing a network. As it was pointed out above, the problem for one pollutant, can be entirely solved using mass exchange network technology, as it was developed by the group led by Professor Manousiouthakis from UCLA.

3.2. Targeting for fresh water usage

The targeting graphical method exploits the idea of plotting the cumulative exchanged mass versus composition for a set of rich and lean streams, a concept first presented by El-Halwagi and Manousiouthakis (1989) for synthesizing mass exchanger networks. Wang and Smith (1994a) proposed a methodology that can effectively pick optimal reuse solutions. Dhole, Ramchandani, Tainsh and Wasilewski (1996) popularized this methodology calling it the ‘water pinch’. The method is based on assuming:

- Constant pollutant load picked up in each process. This is a fair simplifying assumption.
- Maximum inlet and outlet concentrations in each process. These are dictated by solubility, flow rate limitations, fouling.

By combining all these streams in one unique profile, a water limiting profile can be obtained, as it is shown in Fig. 3 for four processes. The fresh water line touches the composite curve at the pinch point and determines the overall water consumption. Once the target flow rate is obtained, a preliminary network is developed using a matching procedure, which is briefly illustrated next. Consider the data given in Table 1.

Wang and Smith (1994a) proposed two techniques: ‘maximum driving forces’ and ‘minimum number of water sources’. The first one showed some limitations and will not be discussed further. The first step of the

Table 1
Example from Wang and Smith (1994a)

Process number	Contaminant load (kg h^{-1})	C_{in}^{max} (ppm)	C_{out}^{max} (ppm)
1	2.0	0	100
2	5.0	50	100
3	30.0	50	800
4	4.0	400	800

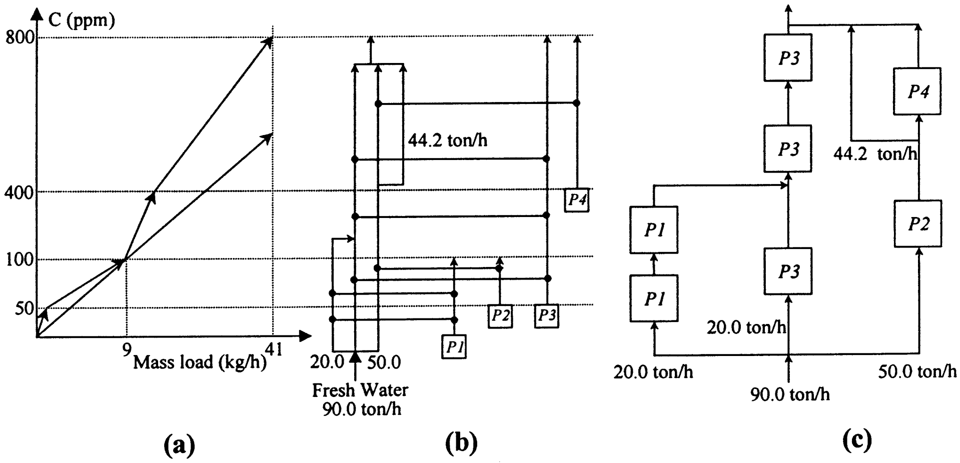

Fig. 4. Single contaminant design grid procedure (following Wang & Smith, 1994a).

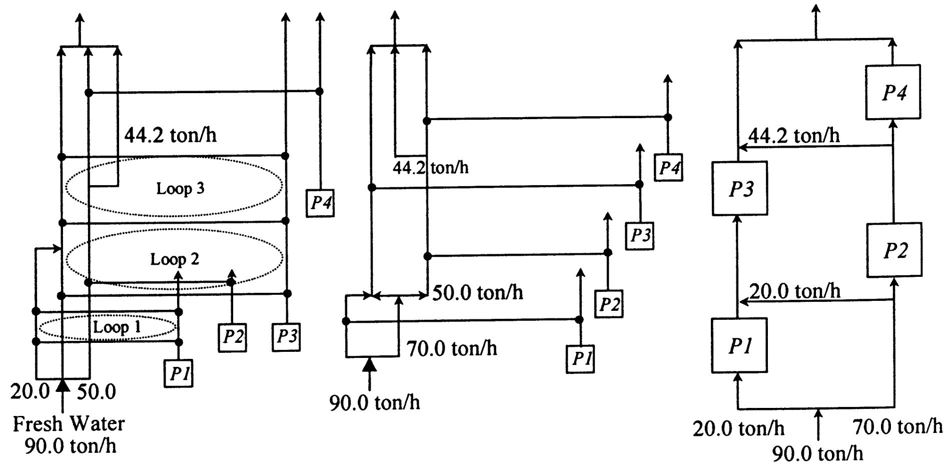

Fig. 5. Loop breaking (following Wang & Smith, 1994a).

minimum number of water sources method is the construction of the design grid, as shown in Fig. 4(b) from which a network can be obtained (Fig. 4(c)). The basis of the procedure is rooted in the work of Linnhoff and Hindmarsh (1983) and Wood, Wilcox and Grossmann (1985).

This design grid contains mixing in the middle of processes, a solution that is clearly not acceptable. To overcome this difficulty, Wang and Smith (1994a) propose a loop breaking technique, which eliminates bypassing and mixing. Fig. 5 shows the loop and the result of the breaking procedure. We omit further explanation of this method as it is well known.

In a follow-up paper, Wang and Smith (1995), showed how the above method can be adapted to consider constraints on the flow rate used for each process as well as water losses. Nevertheless, the loop breaking proposed by Wang and Smith (1994a) is rather difficult to implement for large systems. The difficulty stems from the realization that there is no clear criteria as of which is the loop that needs to be broken at each step. To overcome this difficulty, Olesen and Polley (1997) proposed a simplified design procedure for single contaminant. The authors used the water pinch to obtain the minimum flow rate target and then obtained the network by inspection. However, as stated by the authors, this approach cannot handle more than four or five operations.

Kuo and Smith (1998) also recognized the complexity of the evolutionary design procedure proposed earlier by Wang and Smith (1994a). In an effort to simplify the previous method, the authors introduced a new graphical approach. In addition, they addressed the optimal allocation of fresh water in combination with the distribution of quality of the wastewater that is to be treated. The method consists on identifying the pockets that can be created by successively bending the water supply line upwards. The next step is to create a water 'main' at the end of each pocket and identify processes that should be fed by these mains. Since some processes exist in different regions separated by these mains, a merging needs to take place. This method has some limitations.

For example, when several processes below the pinch have maximum inlet concentration larger than zero, it is not quite simple to identify which process needs to be fed using fresh water first and to what process each wastewater has to be sent. This was clarified later by Savelski and Bagajewicz (1999a,b, 2000a) by introducing the concept of monotonicity in the process-to-process connections. In addition, Gómez, Savelski & Bagajewicz (2000) provided an algorithmic procedure to address this matter.

3.3. Multicomponent systems

Wang and Smith (1994a) also attempted to address a targeting and network design procedure for the case of multicomponent systems. Targeting proved to be very cumbersome, as it required elaborate special shifting of streams in the concentration–load diagram. The method proved to have limitations as it fails to identify optimal solutions. Liu (1999) presented a few interesting heuristic rules. Although some of them are incorrect, the solution procedure has remarkable simplicity and provides good sub-optimal (and sometimes optimal) solutions.

3.4. Data gathering

While all the above methods and the mathematical programming approaches have various degrees of success in solving the problem, data gathering and establishing proper constraints (maximum inlet and outlet concentrations) is a practical problem that has not yet been addressed fully. The designer starts with uncertain data, that is, not knowing well what are the acceptable water specifications for each process. Some of these specifications, nevertheless are fairly straightforward. For example, maximum outlet concentrations are related to solubility and some maximum inlet specifications are process restrictions. In addition, once maximum outlet concentrations are established, inlet maximums can be obtained from the information on the load and the minimum flow rate the equipment can handle. Knowledge of the load is also an issue and in practice cannot be inferred directly. The issue of uncertainty is further discussed later.

3.5. Mathematical programming procedures

After the pioneering work of Takama et al. (1980) no journal publication addressed a mathematical programming formulation of the problem for several years. However, Doyle and Smith (1997) and more recently Alva-Argáez, Kokossis and Smith (1998a,b) and Alva-Argáez et al. (1999) as well as Huang, Chang, Ling and Chang (1999) presented MINLP or NLP models. Work performed related to single contaminant systems is reviewed first.

Savelski and Bagajewicz (2000a) showed that the model for single component can be linearized. Indeed, assume that each water-using unit is characterized by a contaminant load that needs to be entirely removed and by inlet and outlet maximum concentration constraints. Then, the following NLP formulation results:

$$\left.\begin{array}{ll}
\min \sum_j F_j^w & \\
s.t. & \\
F_j^w + \sum_i F_{i,j} - \sum_k F_{j,k} - F_{j,\text{out}} = 0 & \forall j \in \boldsymbol{N},\ i \in \boldsymbol{P}_j,\ k \in \boldsymbol{R}_j \\
F_h^w - \dfrac{L_h}{C_{h,\text{out}}^{\max}} = 0 & \forall h \in \boldsymbol{H} \\
\sum_i F_{i,j}(C_{i,\text{out}} - C_{j,\text{in}}) - F_j^w C_{j,\text{in}} = 0 & \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P}_j \\
\sum_i F_{i,j}(C_{i,\text{out}} - C_{\text{out}}) - F_j^w C_{j,\text{out}} + L_j = 0 & \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P}_j \\
C_j \le C_j^{\max} & \forall j \in \overline{\boldsymbol{H}} \\
C_i \le C_i^{\max} & \forall i \in \boldsymbol{P}_j
\end{array}\right\} \tag{1}$$

3.6. Necessary conditions of optimality

The following necessary conditions of optimality have been developed by Savelski and Bagajewicz (1999a,b, 2000a).

- *Maximum outlet concentrations*: If a solution of the water allocation problem is optimal then all fresh water-using processes reach their maximum possible outlet concentration. Degenerate solutions with lower outlet concentrations but the same overall freshwater consumption may exist. However, these degenerate solutions are such that the flow rate through some processes is larger. Thus, they are not preferred.
- *Concentration monotonicity*: If a solution to the water allocation problem is optimal, then at every process, the outlet concentrations are not lower than the concentration of the combined wastewater stream coming from all the precursors. In other words, given a process j, then $C_{i,\text{out}} \ge C_{P_j,i}$, where $C_{P_j,i}$ is the concentration of the combined wastewater of all the precursors.

The set of interconnections of interest are presented in Fig. 6, omitting others that are not relevant to this case.

3.7. Linear programming

Problem (1) has bilinear terms in flow rate and concentration. These bilinearities can be eliminated using the necessary condition of maximum outlet concentrations, that is, setting outlet concentrations to their maximum values.

The constraints can now be combined as follows:

$$\left.\begin{array}{c}\sum_i F_{i,j}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{in}}) - F_j^w C_{j,in} = 0 \\ C_{j,\mathrm{in}} \le C_{j,\mathrm{in}}^{\max}\end{array}\right\} \Leftrightarrow$$

$$\left\{\sum_i F_{i,j}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{in}}^{\max}) - F_j^w C_{j,\mathrm{in}}^{\max} \le 0 \quad \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P}_j \right. \qquad (2)$$

The resulting linear problem is

$$\left.\begin{array}{ll}
\min \sum_j F_j^w & \\
\text{s.t.} & \\
F_j^w + \sum_i F_{i,j} - \sum_k F_{j,k} - F_{j,\mathrm{out}} = 0 & \forall j \in \boldsymbol{N},\ i \in \boldsymbol{P}_j,\ k \in \boldsymbol{R}_j \\
F_h^w - \dfrac{L_h}{C_{h,\mathrm{out}}^{\max}} = 0 & \forall h \in \boldsymbol{H} \\
\sum_i F_{i,j}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{in}}^{\max}) - F_j^w C_{j,\mathrm{in}}^{\max} \le 0 & \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P}_j \\
\sum_i F_{i,j}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{out}}^{\max}) - F_j^w C_{j,\mathrm{out}}^{\max} + L_j = 0 & \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P}_j
\end{array}\right\} \qquad (3)$$

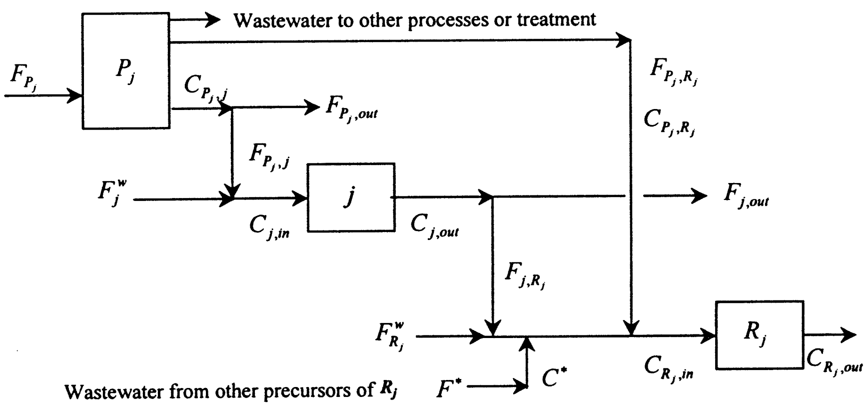

Fig. 6. Precursor and receivers of a process.

Table 2
Limiting data for a ten-processes problem

Process number	Mass load of contaminant (kg h^{-1})	$C_{\mathrm{in}}^{\max}$ (ppm)	$C_{\mathrm{out}}^{\max}$ (ppm)	Minimum fresh water flow rate without reuse (ton h^{-1})
1	2.0	25	80	25.0
2	2.88	25	90	32.0
3	4.0	25	200	20.0
4	3.0	50	100	30.0
5	30.0	50	800	37.5
6	5.0	400	800	6.25
7	2.0	400	600	3.3333
8	1.0	0	100	10.0
9	20.0	50	300	66.6667
10	6.5	150	300	21.6667
		Total minimum flow rate (ton h^{-1})		252.4167

Table 3
Solution of the ten-processes problem

Process number	$F_{i,j}$ (ton h^{-1})	Minimum fresh water flow rate with reuse (ton h^{-1})	Wastewater flow rate (ton h^{-1})
1	0.0	25.0	0.0
2	0.0	32.0	0.0
3	$F_{1,3} = 7.14286$	15.7143	0.0
4	$F_{1,4} = 17.8571$	26.4286	0.0
5	$F_{4,5} = 20.0$	20.0	40.0
6	$F_{7,6} = 4.16667$, $F_{10,6} = 8.33333$	0.0	12.5
7	$F_{3,7} = 4.02857$, $F_{10,6} = 1.29524$	0.0	1.15714
8	0.0	10.0	0.0
9	$F_{2,9} = 32.0$, $F_{4,9} = 11.20$	36.80	78.7048
10	$F_{3,10} = 18.8286$, $F_{4,10} = 13.0857$, $F_{8,10} = 10.0$	0	33.5710
Total minimum freshwater usage (ton h^{-1})		165.9424	

The optimal water flow rate and a feasible realizing network are now both simultaneously obtained. Furthermore, when setting up the problem, the number of variables can be reduced by not including non-monotone connections as suggested by the monotonicity necessary condition. This will become an advantage when other MILP models are used.

3.7.1. Illustration: targeting the fresh water usage

Consider the problem given in Table 2, which involves ten water-using processes. After monotonicity is applied, the number of feasible interconnections reduces from 72 to 40. Table 3 shows the results and Fig. 7 shows the resulting realizing network.

The fresh water savings are over 34%. It is worth noting that the optimization may render a network that, although feasible, could require too many interconnections. Moreover some of them may be even impractical. For example, the flow rate from process 9–7 is only 1.2952 ton h^{-1}, which requires a 15-mm ID pipe, if an economical velocity of 2.0 m s^{-1} is assumed. In this example, there are a total of 12 interconnections among processes and 24 when counting connections from the fresh water source to the processes and connections from the units to the wastewater treatment plant.

3.8. MILP formulations

Once the target is obtained different network alternatives can be sought. To do that, different objective functions are proposed and the minimum fresh water usage is added as a constraint. These objective functions are:

- minimum number of interconnections;
- minimum fixed cost of interconnections;
- compulsory/forbidden matches.

We now consider the case of minimum number of interconnections. Consider the following constraint:

$$F_{i,j} - UY_{i,j} \leq 0 \quad \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P}_j \tag{4}$$

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

$$\sum_j F_j^w = \alpha \tag{5}$$

Thus, the MILP model is (Savelski and Bagajewicz, 2000c):

$$\left.\begin{array}{ll}
\min\left(\sum_{i,j} Y_{i,j} + \sum_{w,j} Y_{w,j} + \sum_{j,o} Y_{j,o}\right) & \\
\text{s.t.} & \\
F_j^w + \sum_i F_{i,j} + \sum_k F_{j,k} - F_{j,\mathrm{out}} = 0 & \forall j \in \boldsymbol{N},\ i \in \boldsymbol{P_j},\ k \in \boldsymbol{R_j} \\
\sum_j F_j^w = \alpha & \text{where } \alpha \text{ is the targeted fresh water} \\
F_h^w - \dfrac{L_h}{C_{h,\mathrm{out}}^{\max}} = 0. & \\
\sum_i \boldsymbol{F_{i,j}}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{in}}^{\max}) - F_j^w C_{j,\mathrm{in}}^{\max} \leq 0 & \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P_j} \\
\sum_i \boldsymbol{F_{i,j}}(C_{i,\mathrm{out}}^{\max} - C_{j,\mathrm{out}}^{\max}) - F_j^w C_{j,\mathrm{out}}^{\max} + L_j = 0 & \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P_j} \\
F_{i,j} - UY_{i,j} \leq 0 & \forall j \in \overline{\boldsymbol{H}},\ i \in \boldsymbol{P_j} \\
F_j^w - UY_{w,j} \leq 0 & \forall j \in \overline{\boldsymbol{H}} \\
F_{j,out} - UY_{j,o} \leq 0 & \forall j \in \boldsymbol{N} \\
Y_{i,j}; Y_{w,j}; Y_{j,o} = 0, 1 &
\end{array}\right\} \tag{6}$$

The solution for the problem of Table 2 is shown in Fig. 8.

Reducing the number of interconnections is relevant for a cost-effective design. However, the networks obtained in previous examples do not guarantee minimum cost but only minimum number of connections. Since not all interconnections will require the same fixed capital investment, it seems most appropriate to minimize the fixed annualized cost. The cost coefficients can

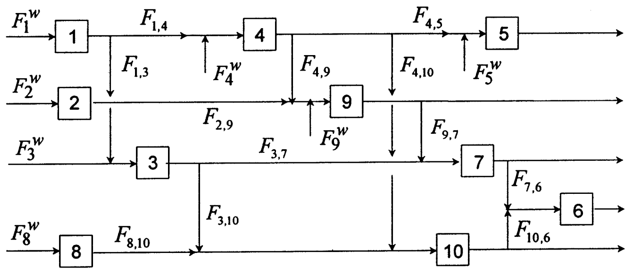

Fig. 7. Solution network for the ten-processes problem (LP formulation).

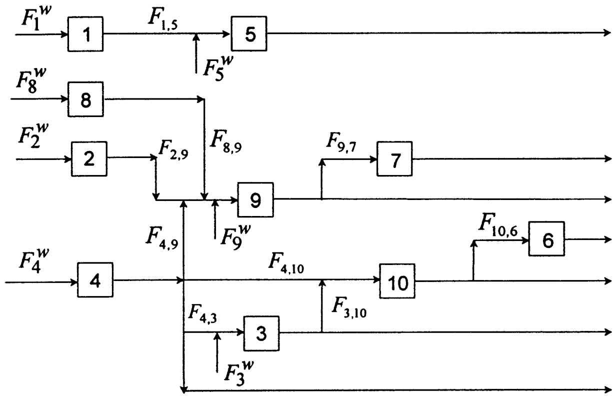

Fig. 8. Minimum number of interconnections (MILP formulation).

Table 4
Limiting data for Example 5 from Olesen and Polley (1997)

Process number	Contaminant load (kg h^{-1})	$C_{\text{in}}^{\max}$ (ppm)	$C_{\text{out}}^{\max}$(ppm)
1	2.0	25	80
2	5.0	25	100
3	4.0	25	200
4	5.0	50	100
5	30.0	50	800
6	4.0	400	800

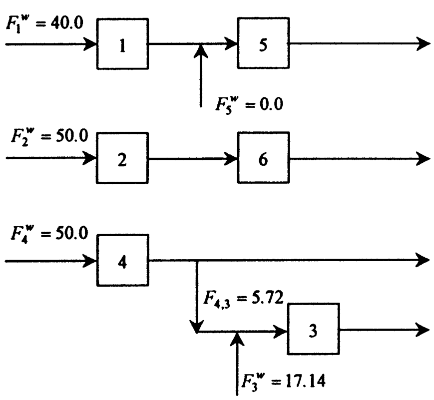

Fig. 9. Network proposed by Olesen and Polley.

be understood as the corresponding calculations of the annualized installed costs of piping, valves and pumps. The new objective function can be written as:

$$\sum_{i,j} c_{i,j} Y_{i,j} \tag{7}$$

It is quite often found that connections between certain processes are not allowed or must be imposed due to design or retrofit strategies. For example: heating and/or cooling limitations may render certain connections beneficial or undesirable; low flow rate interconnections, typically below 2.0 m^3 h^{-1}, may be discarded due to economical or controllability reasons; finally, distance and space limitations may become decision variables as well. When imposing such restrictions to any of the previous cases we can expect either feasible or infeasible solutions. The infeasibility may arise because no network can be found for the fresh water flow rate fixed at its minimum target.

3.9. Use of degeneracy

Although the previous examples provide different alternatives, they are all built assuming that the outlet concentrations are at their maximum values. There are, however, solutions to the problem that satisfy the target minimum fresh water usage, but have outlet concentrations lower than their maximum. The existence of these degenerate solutions can be used to reduce the number of connections even further.

Consider the example problem proposed by Olesen and Polley (1997) (Table 4).

The authors solved this problem by inspection and proposed the network solution illustrated in Fig. 9. The reported fresh water target is 157.14 ton h^{-1}. From this figure, it can be observed that Process 1 is consuming 15.0 ton h^{-1} more fresh water than the minimum required to pickup its entire load. As a consequence, its outlet concentration is 50 ppm instead of its possible maximum of 80 ppm. Therefore, the solution offered by Olesen and Polley can be understood as a degenerate solution. Its equivalent is the same network where process 1 reaches its maximum outlet concentration and $F_1^w = 25.0$, $F_5^w = 15.0$, with the rest of the values being the same. The wastewater produced by Process 1 would be at 80 ppm.

One can explore degenerate solutions where the fresh water intake of either Process 3 or 4 is eliminated. Consider the solution obtained using the LP model (Fig. 10(a)). Assume now that one wants to eliminate the fresh water connection to Process 3. In this case wastewater available at 25 ppm or lower can be used (25 ppm is the maximum inlet concentration allowed for Process 3). To do that, the fresh water intake to Process 1 should be increased to 80.0 ton h^{-1}. The minimum necessary reuse between units 1 and 3 is 22.86 ton h^{-1}. The remaining wastewater at process 1, 57.14 ton h^{-1} can then be sent to Process 4 reducing its fresh water needs to 7.14 ton h^{-1}. Thus, a new equivalent and feasible network can be obtained by increasing F_1^w,

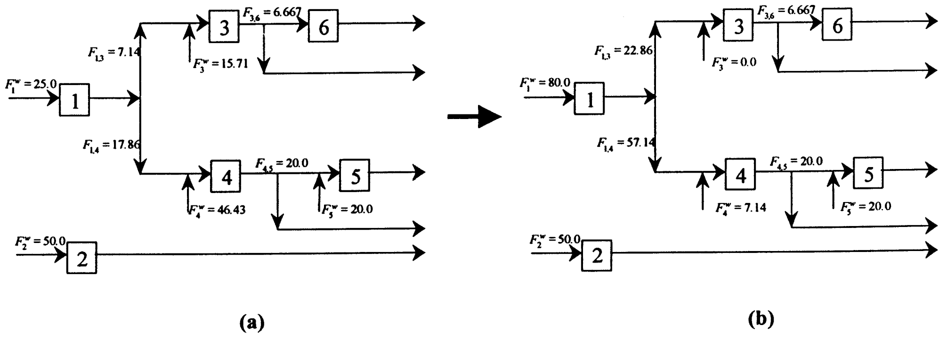

Fig. 10. Degenerate alternatives for the Olesen and Polley problem (Table 4).

reducing F_4^w and eliminatingF_3^w. The alternative flow rates are shown in Fig. 10.

3.10. Multicontaminant systems

Doyle and Smith (1997) proposed to solve the multicomponent version of (1) using an iterative procedure as follows: One can first construct a linear problem by assuming that all contaminants are at their maximum outlet concentration, that is $C_{p,h,\mathrm{out}} = C^{\max}_{p,h,\mathrm{out}}$. In addition, to make the problem feasible, they propose to relax the component balance as follows:

$$\sum_i F_{i,j}(C^{\max}_{p,i,\mathrm{out}} - C^{\max}_{p,j,\mathrm{out}}) - F_j^w C^{\max}_{p,j,\mathrm{out}} \leq L_{p,j} \tag{8}$$

With the solution of such LP problem they propose to solve the NLP multicomponent version of (1). To aid in the search for such solutions, they propose to add several other constraints on maximum flows of wastewater that can go from one process to another. To illustrate their procedure, they present the data of Table 5. They obtained the sub-optimal solution of Fig. 11.

Alva-Argáez et al. (1998a,b) presented a solution approach for multiple contaminant systems in combination with water treatment in which they include piping costs as well as treatment costs. One can however, use their model to solve the problem for the water allocation only. The objective function that they propose for the water allocation problem is:

$$\alpha \sum_{i,j} C_{i,j} Y_{i,j} + \beta \sum_i F_i^w \tag{9}$$

where α and β are appropriate annualization factors. They use the same relaxation as in (8), but in this case they solve the problem by adding a penalty function consisting of the summation of all the slack variables coming from (8). Thus, the linear problem can be solved to obtain a network of flows, which in turn can be used to obtain a new set of concentrations. These concentrations are substituted in (8) again, until convergence is achieved. This is the same procedure that Takama et al. (1980) used. The sequence of MILP obtained is a sequence of infeasible problems. At the end, the authors claim that: (a) the sequence converges, and in such case; (b) the solution is near optimal. Global optimality is, of course, not guaranteed.

Recently, Benko, Rev, Szitkai and Fonyo (1999) modeled the example problem proposed by Takama et al. (1980) as a non-convex MINLP problem. The authors updated the concentration limits in the desalter to make the problem more realistic. This approach cannot guarantee optimality and numerical limitations may limit its use to small-scale problems. Finally, Alva-Argáez et al. (1999) discuss some trans-shipment models based on several assumptions, some of them restrictive.

Table 5
Example from Wang and Smith (1994a)

Process number	Contaminant	$C^{\max}_{\mathrm{in}}$ (ppm)	$C^{\max}_{\mathrm{out}}$ (ppm)
1	Hydrocarbon	0	15
	H_2S	0	400
	Salt	0	35
2	Hydrocarbon	20	120
	H_2S	300	12 500
	Salt	45	180
3			
	Hydrocarbon	120	220
	H_2S	20	45
	Salt	200	9500

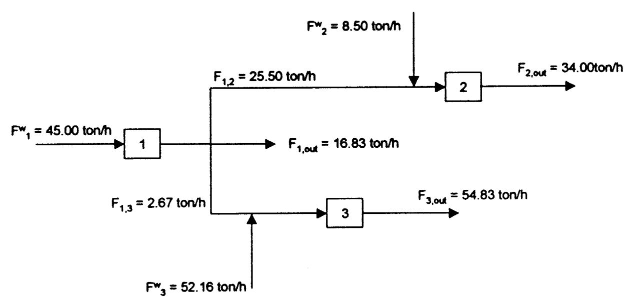

Fig. 11. Solution of the problem of Table 5.

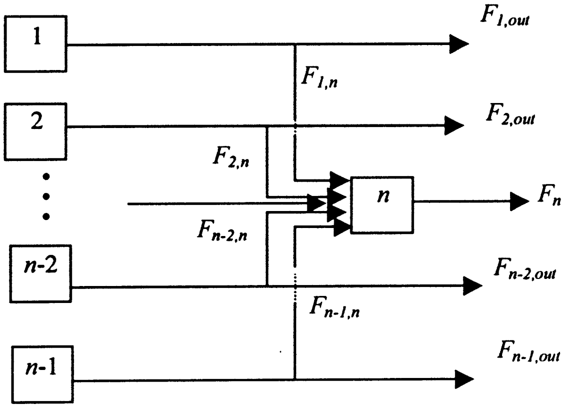

Fig. 12. Connections from precursors of process n.

3.11. Necessary conditions of optimality for multicontaminant systems

Savelski and Bagajewicz (2000d) derived necessary conditions of optimality for multicontaminant systems. These necessary conditions are very similar to the above-presented necessary conditions for single components. The condition of maximum outlet concentration is replaced by a condition of at least one component reaching its maximum. The monotonicity condition is replaced by a monotonicity of key components. These key components are defined as those components that reach their maximum concentration first when fresh water is used. These conditions are used later in an algorithmic design procedure. In some systems, the source of water is not contaminant free, and therefore these necessary conditions need to be modified.

3.12. Algorithmic design procedures

This approach is very recent and relies on necessary and sufficient conditions of optimality for single component systems (Savelski & Bagajewicz, 1999a, 2000b). The necessary conditions have been outlined above. This non-targeting and non-iterative design procedure efficiently solves the water allocation problem when a single component is present. Furthermore, the method can be totally performed by hand in the case of single contaminant problems regardless of problem size. The maximum reuse rules, which are the basis of the method and part of the sufficient conditions, are introduced first.

3.13. Maximum reuse rules

These rules are used to calculate the amount of wastewater that a process can receive from its precursors in such a way that the amount of fresh water consumed is minimized.

Consider a set of $(n-1)$ precursors of process n (Fig. 12). We assume that process n has a maximum outlet concentration that is larger than that of all its precursors (monotonicity). In Fig. 12, all possible connections from the precursors of process n are shown.

Without loss of generality, assume that the outlet concentrations of all these processes are ordered monotonically.

$$C_{1,\mathrm{out}}^{\max} \leq C_{2,\mathrm{out}}^{\max} \leq \ldots\ldots\ldots \leq C_{n-1,\mathrm{out}}^{\max} \leq C_{n,\mathrm{out}}^{\max} \tag{10}$$

Savelski and Bagajewicz (1999a, 2000a) showed that, in the case where the fresh water usage is not zero, then this minimum is obtained by allocating as much wastewater from the precursors with the smallest outlet concentration possible, that is

$$F_{1,n} = F_1, F_{2,n} = F_2, \ldots, F_{s,n} \leq F_s, F_{s+1,n} = 0, \ldots, F_{n-1,n} = 0 \tag{11}$$

where the $F_{s,n}$ is obtained by setting the inlet concentration to process n to its maximum value. In the extreme case, all wastewater from all processes are sent to process n and the inlet concentration is lower than the maximum.

In the case of wastewater users, that is, when the fresh water usage of process n is zero, a different rule is used. When some precursors have outlet concentrations higher than the maximum inlet concentration of process n ($C_{j,\mathrm{out}}^{\max} \leq C_{n,\mathrm{in}}^{\max}$ $j = 1, \ldots, k$ and $C_{j,\mathrm{out}}^{\max} > C_{n,\mathrm{in}}^{\max}$ $j \geq k + 1, \ldots, n-1$), then, linear combinations of available wastewater of concentration higher and lower than $C_{n,\mathrm{in}}^{\max}$ can be formed. The precursors with $C_{i,\mathrm{out}} \leq C_{n,\mathrm{in}}^{\max}$ can be seen as pseudo-fresh water sources. The precursors with $C_{i,\mathrm{out}} > C_{n,\mathrm{in}}^{\max}$ can then be considered as the actual reusable wastewater sources. Thus, the first k wastewater streams can be considered as 'good quality' precursors because they can be used to dilute the rest, which could not otherwise be used. If the wastewater user under consideration were the last process to be analyzed, then the assignment of water would not really affect the total water intake. However, when some receivers downstream of process n are fresh water users, then the quality of the wastewater available needs to be preserved so that these other fresh water receivers downstream receive the cleanest wastewater possible. This heuristic is always true. Thus, the problem of assigning water to a wastewater user is analogous to that of the fresh water users. Savelski and Bagajewicz (2000b) proposed appropriate LP problems to formally obtain reuse rules. Two cases exist:

- Case I: All precursors are pseudo-fresh water sources. $C_{n-1,\mathrm{out}}^{\max} < C_{n,\mathrm{in}}^{\max}$: In this case, the reuse rule states that the dirtiest water is used first and, if it is not enough, water of the next highest concentration is used until all requirements are fulfilled.
- Case II: Only some precursors are pseudo-fresh water sources; i.e.

$$C_{i,\mathrm{out}}^{\max} \leq C_{n,\mathrm{in}}^{\max} \quad \forall i \leq k, \; C_{i,\mathrm{out}}^{\max} > C_{n,\mathrm{in}}^{\max} \quad \forall i > k \tag{12}$$

The optimal reuse pattern is obtained as a combination of the dirtiest set of pseudo-fresh water precursors possible and the cleanest set of wastewater available. Fig. 13 illustrates one such generic combination.

In this scheme, pseudo-fresh waters from process s ($s < k$) to process k are used to dilute wastewater from process ($k + 1$) to process t ($t > k$). Once the partial wastewater providers s and t are identified, the following flow rates are obtained, the rest being zero.

$$F_{j,n} = F_j \quad \forall j = (s+1), \ldots, (t-1), \quad F_{s,n} < F_s, F_{t,n} < F_t \tag{13}$$

The flow rates $F_{s,n}$ and $F_{t,n}$ can be obtained by requesting that the inlet and outlet concentrations be equal to their corresponding maximum values.

3.14. Sufficient conditions and algorithm

Savelski and Bagajewicz (2000b) defined a maximum reuse structure as a flowsheet that satisfies the property that all inlet wastewater flows to any unit are obtained using the maximum reuse algorithm. They proved using mathematical induction that a maximum reuse structure is optimal.

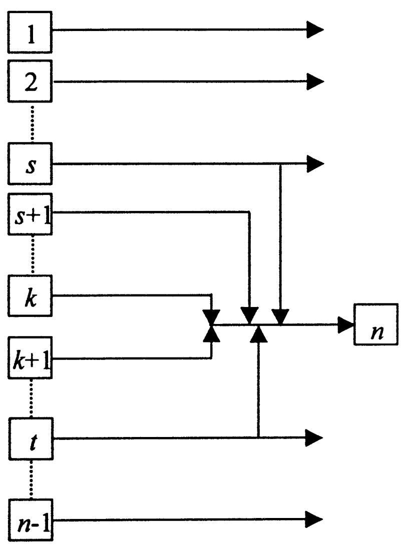

Fig. 13. Optimal reuse pattern.

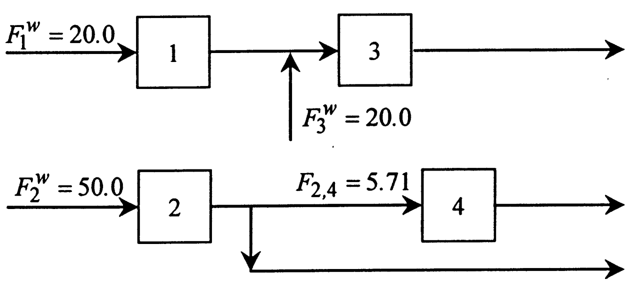

Fig. 14. Solution of the algorithmic procedure.

Based on these sufficient conditions, the algorithm is constructive. It starts identifying head processes and then picks a wastewater receiver according to monotonicity. Once the maximum reuse rule is applied, the next process is picked, continuing in this way until all processes are added to the flowsheet. The procedure guarantees global optimality and does not require a targeting phase as it provides simultaneously the minimum fresh water consumption and the network. A final worthwhile remark: the procedure provides only one of the very many solutions that this problem may have.

Illustration: The example is taken from Wang and Smith (1994). The system involves four processes and their corresponding data is given in Table 1. We now apply the algorithm.

3.14.1. Step 1: identify head processes

Process 1 is the only process with maximum inlet concentration equal to zero. The fresh water is given by:

$$F_1^w = \frac{L_1}{C_{1,\mathrm{out}}^{\max}} = \frac{2000 \text{ g h}^{-1}}{100 \text{ ppm}} = 20.0 \text{ ton h}^{-1}$$

3.14.2. Step 2: maximum outlet concentration ordering

There are three processes left to order. Process 2 goes first in the list, as its outlet concentration is 100 ppm. The other two processes have outlet concentration of 800 ppm, and therefore can be put in any desired order.

3.14.3. Step 3: Apply the maximum reuse rules

The first process of the list (Process 2) is taken and the rule is applied. Due to the necessary condition of monotonicity, there are no possible precursors for this process. Therefore, fresh water is fed to Process 2. The fresh water intake is $F_2^w = 50.0$ ton h^{-1}.

The rule is applied to Process 3 now. The maximum outlet concentration of this process allows to supply it with wastewater from either Process 1 or 2. A simple calculation gives: $F_1 = F_{1,3} = 20.0$ ton h^{-1}. Consequently, the water intake of Process 3 can be fulfilled by using Process 1 only. The necessary fresh water intake is: $F_3^w = 20.0$ ton h^{-1}.

Finally, Process 4 is considered. This process has only one monotone precursor, which is Process 2. Process 3 has wastewater of the same concentration as the maximum outlet Process 4. Therefore, it cannot be used as a wastewater provider. The outlet concentration of Process 2 is lower than the maximum inlet concentration of Process 4, therefore the latter is a wastewater user candidate (Case I). Thus one obtains $F_{2,4} = 5.7143$ ton h$^{-1} < F_2$. Process 4 does not require any other water intake to fulfill its requirements. Consequently, it is a true wastewater user and the problem is solved.

The total fresh water intake is: $W = F_1^w + F_2^w + F_3^w = 20.0 + 50.0 + 20.0 = 90.0$ ton h^{-1}. Both, the water consumption and the network design (Fig. 14) coincide with those reported by Wang and Smith (1994).

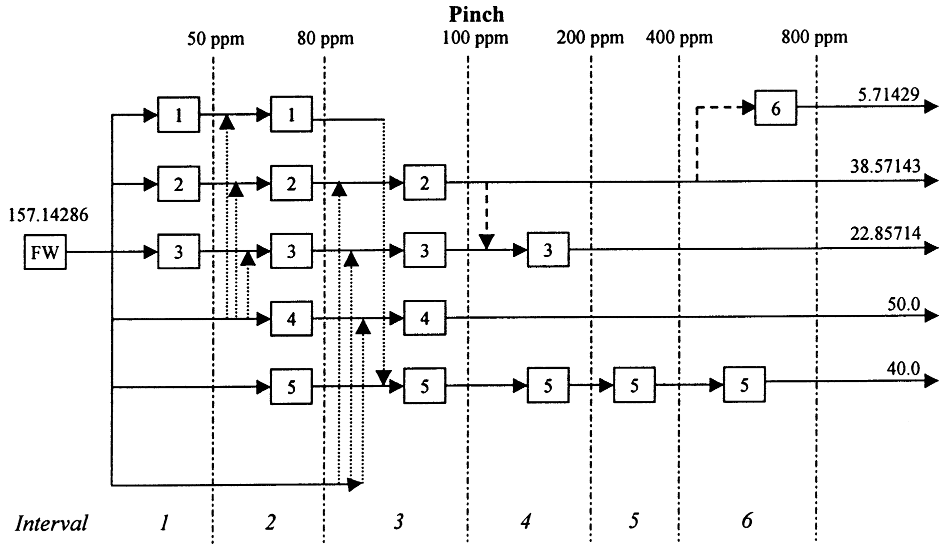

Fig. 15. Initial allocation of fresh water.

3.15. Concentration grid algorithm

Another algorithmic procedure was developed by Gómez et al. (2000), which can also be implemented by hand, even for large systems. This procedure is based on the construction of a concentration grid, similar to the one proposed by Wang and Smith (1994a). After the minimum fresh water is determined, the method requires that a concentration grid, based on maximum inlet and outlet concentrations be constructed. All processes are allocated within this grid such that they appear in as many intervals as their respective inlet and outlet maximum concentrations span through. Fig. 15 illustrates the allocation of fresh water at each interval in each of the processes for the Olesen and Polley problem (Table 4). The second step requires assigning all the available fresh water to all fresh water users. The amount of water supplied is only the required to reach the outlet concentration of the first interval. In a third step, wastewater from these processes is assigned to processes in the subsequent intervals as required. Additional fresh water is used as needed.

To assign water from one process to another in any subsequent interval it is necessary to define all the sources available from previous intervals. These sources can be either fresh water, or some wastewater coming from other previous concentration intervals. All processes must reuse their own water. Three different approaches to perform the wastewater allocation can be used. Mixers can be used to collect water from previous intervals and redistribute it. Alternatively, a policy of using the worst quality water available first for subsequent allocation, or the cleanest.

The final step consists of merging the processes into a single one. Such process was suggested first by Kuo and Smith (1998) and proven always feasible by Gómez et al. (2000). The final design of the Olesen and Polley (1997) problem obtained after merging is shown in Fig. 16.

3.16. Branch and bound algorithmic procedure for multicontaminant systems

Consider the case where the pattern of flows is given, that is, all the potential precursors of each process are fixed. In such a case, a generalization of the maximum reuse rule derived for single components consists of an LP sub-problem (Savelski, Rivas & Bagajewicz, 1999; Bagajewicz, Rivas & Savelski, 2000c) proved that. The next step is the construction of a tree of combinations. Such a tree is shown in Fig. 17 and each branch of the tree can be interpreted by saying that every member of the combination is only a precursor of the processes

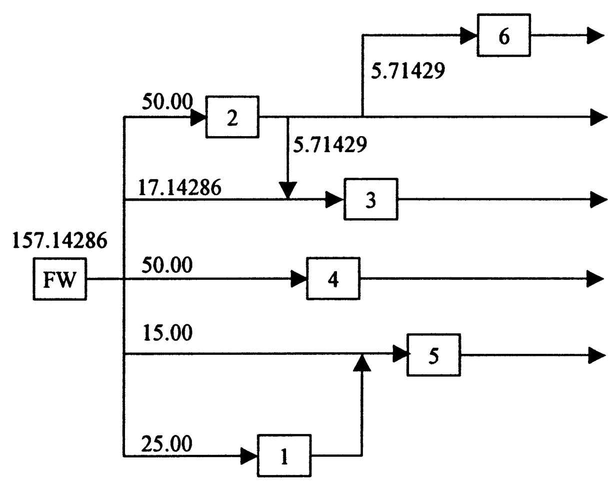

Fig. 16. Final design of the water network for the Olesen and Polley problem.

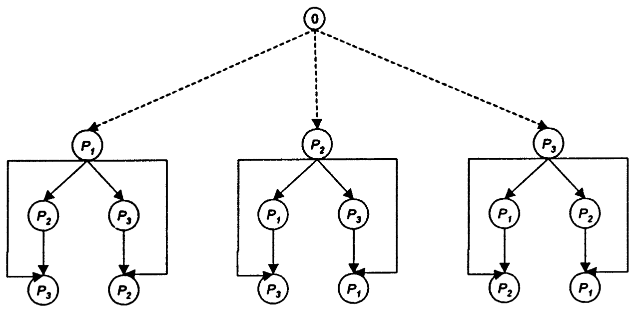

Fig. 17. Tree of alternative sequences.

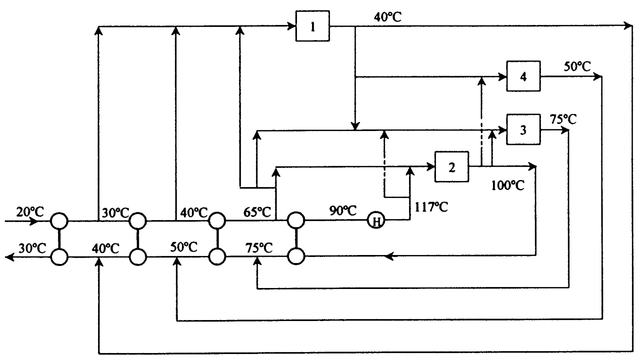

Fig. 18. Heat integrated solution (following Savulescu & Smith, 1998).

that follow in the list. Whenever a node is added to the tree, the LP problem is solved and water/wastewater allocation is obtained.

A first upper bound is obtained by developing one complete branch of the tree. This tree is then explored developing every branch and using stopping criteria. Monotonicity of key components, as well as definitions of fresh water user processes are used as branch cutting criteria. In addition at each node of the tree a partial count of freshwater intake is available, and when it is larger than the current upper bound, it is also used to cut the tree.

Therefore, the search allows exploring different design alternatives, capability that other methodologies fail to provide. Some of these alternative networks may consume more fresh water than the optimal case but they may still present an interesting option if the interconnections among processes are somehow limited. Forbidden and compulsory connections among processes are not unusual. This procedure guarantees global optimality for the case where all the wastewater users are terminal processes.

The method is very efficient. For example, the problem of Table 5 renders the same two processes obtained by Doyle and Smith, and no others. For example, a four processes problem, also presented by Doyle and Smith (1997) has one head process and, monotonicity reduces the problem to only two sequences.

The importance of this method stems from its ability of being able to provide several sub-optimal solutions that may be attractive to the practical engineer, but can also be useful for retrofit studies (Bagajewicz, Rodera & Savelski, 2000b; Bagajewicz et al., 2000c)

3.17. simultaneous water minimization and heat integration

The importance of simultaneous minimization of utility and fresh water usage was first addressed by Savelski, Lingareddy and Bagajewicz (1997). More recently, Savulescu and Smith (1998) proposed a graphical method to solve the minimization of fresh water achieving at the same time the minimum utility target. The approach used is limited to small-scale problems and it requires that all wastewater streams be mixed. Finally, it cannot guarantee the construction of a network featuring minimum number of heat exchangers. The method is in reality a two-stage sequential procedure in which certain heuristics are used in the first stage to obtain a network of process-to-process interconnections such that the indirect heat exchange structure might feature minimum utility. However, these rules cannot guarantee that the resulting structure will be optimal. Finally, the authors assume that there are no process-to-process wastewater connections that require heating or cooling in a heat exchanger. This allows them to introduce a separate systems diagram, which consists on aligning vertically portions of the hot and cold composite curves. Finally, to build the heat exchanger network, it was assumed that the wastewater is merged to be sent as a unique stream to treatment. If one wants to send these streams to water treatment separately, the concept of separate systems has to be re-formulated at the least.

Bagajewicz, Savelski and Rodera (1999a) and Bagajewicz, Rodera and Savelski (2000a) proposed to solve the targeting problem by coupling the linear programming targeting problem given by (3) with a regular transshipment model for heat integration. The solution to this problem provides a heat target. An MILP formulation follows, in which the objective function is the minimum number of units and the same constraints of targeting coupled with match counting constraints follow.

Illustration: Savulescu and Smith (1998) proposed and solved the example of Table 1, with the following additional data: Fresh water temperature: 20°C, Wastewater temperature: 30°C, and temperature of processes, 40, 100, 75, and 50°C, for processes 1, 2, 3, and 4, respectively. The resulting proposed solution is shown in Fig. 18.

The above problem was has at least two alternative solutions, one with heat exchangers involving process-to-process streams. One such solution is shown in Figs.

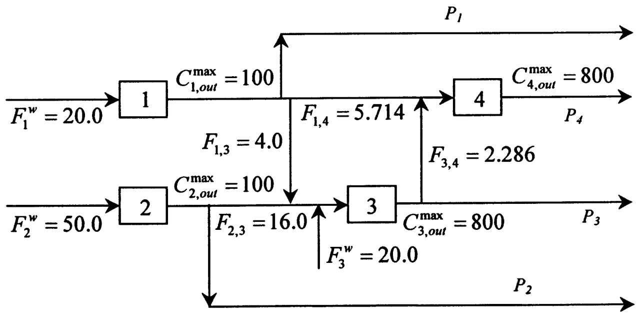

Fig. 19. Water network connections from Bagajewicz et al. (1999a, 2000a).

19 and 20. A simple merging manipulation produces the network of Fig. 21, which has a smaller number of exchangers than the one in Fig. 18.

This procedure shows that graphical procedures cannot tackle the variety of possibilities, in particular the cases when heating is required in process-to-process streams, and cannot effectively solve the problem. In this formulation, the simultaneous water allocation and maximum energy recovery heat exchanger networks are determined simultaneously, including the mixing of streams.

4. Optimal wastewater treatment

As it was outlined above, the optimal design of wastewater systems started with Takama et al. (1980), who solved this problem in conjunction with the water allocation problem. In this section the contributions to

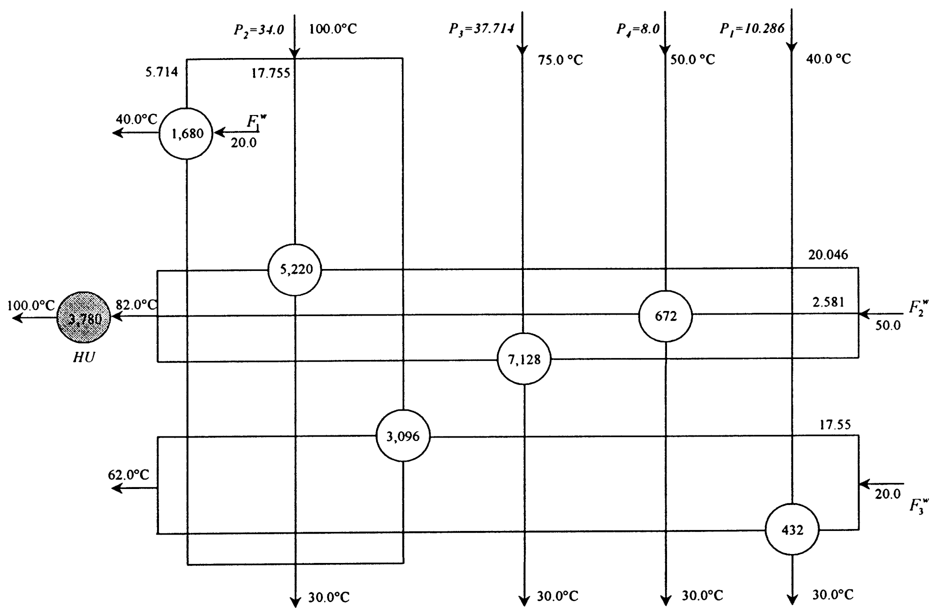

Fig. 20. Heat exchanger network from Bagajewicz et al. (1999a, 2000a).

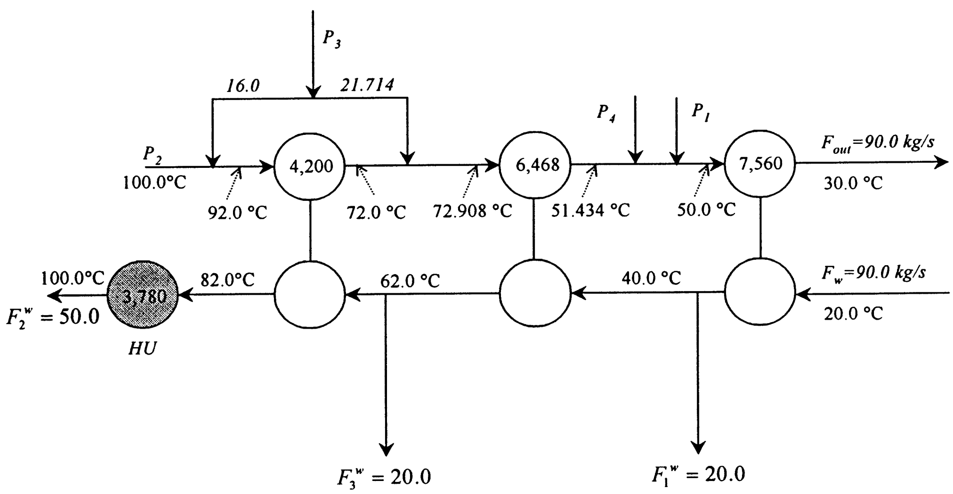

Fig. 21. Heat exchanger network after merging.

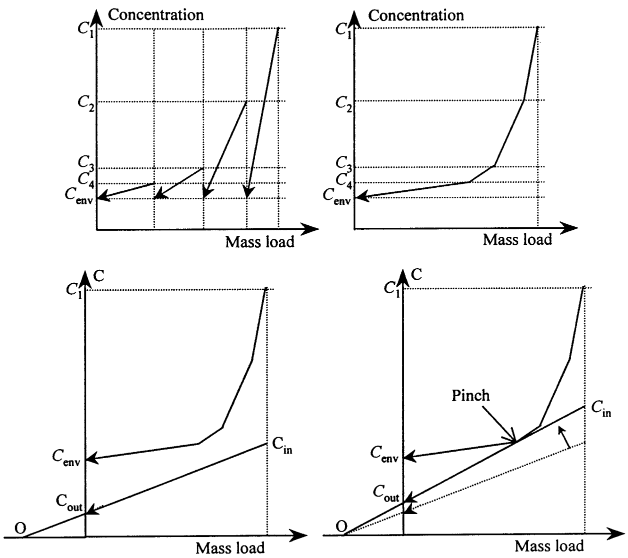

Fig. 22. Optimal regeneration flow rate (following Wang & Smith, 1994b).

the design of wastewater treatment systems only is reviewed. The synergy between the two systems and the efforts to address structures such as those of Fig. 1(d), are discussed in the next section. As noted above, zero liquid discharge solutions have not been attempted directly yet.

4.1. Conceptual design procedures

Wang and Smith (1994b) approached the design of distributed effluent treatment by a similar graphical procedure as presented for the water/wastewater allocation problem. The authors used the same cost functions for the effluent treatment units as those proposed by Takama et al. (1980). The model is based on the following assumptions:

- Several streams available for cleaning can be split and sent to different treatment operations. That is, no merging of these streams is assumed. However, this still implies end-of-pipe treatment, as in Fig. 1(c).
- The flow rate of water through the processes is constant.
- The treatment units have fixed pollutant removal ratio.
- Cost of treatment is assumed proportional to the flow rate of the stream to cleanup. A concentration–load diagram discussion justifies this simplifying assumption.

Once the problem has been put in the framework of Concentration–load diagrams, a composite curve representing all wastewater streams can be constructed. A minimum treatment flow rate is then obtained by assuming a fixed removal ratio. This is accomplished by rotating a treatment flow rate line around point O (Fig. 22).

When cost does not decrease with flow rate, Wang and Smith (1994b) identify a feasible region within which the treatment flow rate line should lie. A classification of streams then follows and certain design rules are used to obtain the network. For the case of multiple contaminants, a network for each contaminant is designed and a merging procedure produces the final unified network. A revised version of this procedure was presented by Kuo and Smith (1997, 1998). A graphical method that utilizes the pinch concept along with what the authors referred to as the wastewater degradation concept. The wastewater degradation takes into account the exergy losses due to the mixing of wastewater streams of different qualities. Then, the authors explored several flowsheet alternatives and choose the network with lower exergy losses. This approach cannot be effectively applied to a system with many contaminants and many wastewater streams. Despite their value in understanding and dissecting the complexity of the problem, these insights have not been proven useful in helping mathematical programming formulations to find global optima. In view of the limitations of this approach it is not expanded further.

Recently, Freitas, Boaventura and Costa (1999) illustrated the use of the hierarchical design approach (Douglas, 1988) to the design of these systems. They constructed a relational database and an expert system to determine the best sequence of treatment processes. The method cannot of course, guarantee any optimality.

4.2. Mathematical programming procedures

In an effort to systematize a solution procedure for this kind of problems and moving away from conceptual design procedures into mathematical programming. Alva-Argáez et al. (1998a,b) modeled the entire water management problem by means of a superstructure, which leads to a MINLP problem that includes some elements not present in previous models. The model considers the presence of water losses, it has bounds on water flow rates and it assumes constant removal ratio in the wastewater treatment units. The objective function is non-linear and the constraints contain the bilinear constraints that arise from component balances. No heat integration is included. Although the model does not guarantee optimality, the authors claim obtaining successful results on a 12 processes and three treatment units. Galán and Grossmann (1998) also solved the effluent-treatment distribution problem using mathematical programming. Finally Huang et al. (1999) propose a similar NLP approach. Their contribution has some more realistic assumptions regarding the outlet concentrations of certain processes and treatment units. They realize that, in some cases, certain units are better modeled if outlet concentrations are considered fixed, instead of fixed loads or fixed removal ratios. Their approach is a simple extension of the one presented by Galán and Grossmann (1998) and has much more merit in the type of examples solved, rather than in the solution procedure.

The solvability of these MINLP problems is at the heart of the challenge. While Alva-Argáez et al. (1998a,b), apply essentially a relaxation procedure similar to the one outlined by Doyle and Smith (1997) to solve the multicomponent water allocation problem (see above), Galán and Grossmann (1998) used tight linear relaxations to obtain good starting point for an NLP solver. At this point, it can be said that the whole area is moving towards mathematical programming methods. A few researchers are still exploiting conceptual insights to simplify solution procedures.

It is important to note that this problem does not have minimum outlet concentrations in the outlet of the treatment process, although maximum at both inlet and outlet can be prescribed. In addition the removal ratio is fixed, not the load. If the load were fixed, the distributed treatment problem would be an exact mirror image of the water allocation problem.

Mass exchanger network (MEN) technology was proposed by El-Halwagi and Manousiouthakis (1990) to solve a special case of phenol removal from refinery wastewater. This approach has not yet been used in combination with other techniques.

5. Simultaneous water allocation and wastewater treatment

Takama et al. (1980) already posed the problem as a simultaneous optimization of the overall usage of water. They however, proposed a superstructure of the type shown in Fig. 1(c). In other words, even though the water treatment is distributed, it is still centralized. Wang and Smith (1994a) showed the value of decentralized treatment, by discussing in detail the benefits of

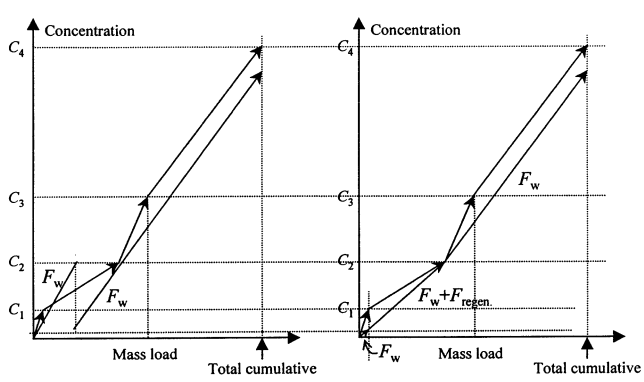

Fig. 23. Water allocation with partial regeneration (following Wang & Smith, 1994a).

partial regeneration of water in the water allocation problem. Their approach is summarized in Fig. 23, where the slope of the target water line can be increased because regeneration takes place, releasing thus the constraint imposed by the pinch. The figure also targets what is the concentration at which regeneration has to take place.

Although Wang and Smith (1994a) were able to identify regeneration opportunities for these systems, the conceptual design procedure for building the network has the same problems as the design without regeneration, especially for multicomponent. No attempt to address decentralized treatment was performed for a while. Kuo and Smith (1998) discussed briefly the effect of the design of the water allocation problem in the type, flow rate and quality of streams that feed the distributed treatment in system of the type of Fig. 1(c).

Alva-Argáez et al. (1998a,b), Benko et al. (1999) and Huang et al. (1999), addressed the whole problem with an MINLP or NLP approach, depending on the case. The advantages of these formulations were discussed above. While it is not clear to what extent Alva-Argáez et al. (1998a,b) used superstructures of the type shown in Fig. 1(d), it is worth pointing out that the other two papers considered these structures in their models. For those that consider the issue of global optimality being of paramount importance, it is worth pointing out that it is not guaranteed by any of these methods. In addition, it is not clear what is the maximum size of problems that can be solved using this approach. It appears however, that realistic sizes can be achieved by sacrificing some nonlinearities.

6. New research opportunities

6.1. Fixed concentrations versus fixed mass loads

Most of the previous work has approached the water reuse problem by assuming that: (1) The water supplied to a process always removes fixed loads of contaminants; and (2) The solubility and corrosion limits can be used to establish maximum inlet and outlet concentration constraints imposed on pollutants. These assumptions came as a necessity to represent complex processes through simplifying approximations, making the problem easier to solve.

Consider briefly a desalter unit (Fig. 24). In this process water is injected (F_w) with salt concentration C_w. The raw crude comes with a certain amount of water (F_{wRi}) and some salt content. The desalted crude leaves the unit with residual water containing salt.

Using material balances, assuming that the water in the crude and the effluent water stream have the same salt concentration and working with a constant salt

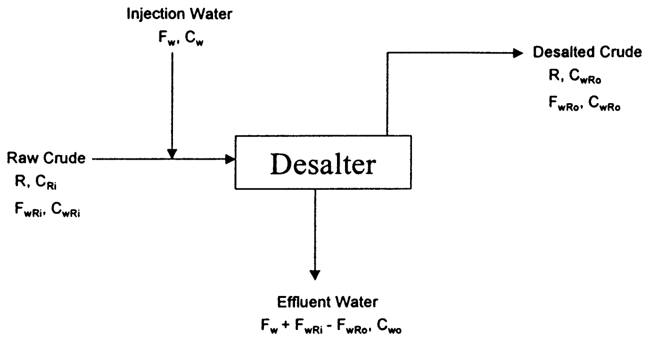

Fig. 24. Balance on a desalter.

removal $(1-\alpha)$ (independent of the flow rate and the concentration of the incoming water), one arrives at the following formula:

$$F_w^2 C_w + F_w Z C_w + F_w(S - RC_{Ro} - \alpha S) + Z(S - RC_{Ro}) - F_{wRi}\alpha S \geq 0 \tag{14}$$

where $Z = F_{wRi} - F_{wRo}$ and $S = RC_{Ri} + F_{wRi}C_{wRi}$. This equation is quadratic in the water flow rate. If the contaminant is salt: $C_{Ri} = C_{Ro} = 0$ and the equation is slightly simplified. It becomes linear in F_w only when freshwater is used ($C_w = 0$). For the case of H_2S instead of salt, one has $K = C_{Ro}/C_{wo}$ and another quadratic equation is obtained. Fig. 25 shows the impact of these equations in the typical concentration vs. load diagram used by Wang and Smith (1994a) and subsequent papers. In Fig. 25(a), the diagram proposed by Wang and Smith (1994a) is shown. This contrasts with Fig. 25(b), where the load and the exit concentration vary with the flow rate used.

The problem is even richer in alternatives. In some other systems contaminants may reach solubility limits, in which case the outlet concentration is fixed and the load is, once again, variable with the flow rate. In addition, temperature and pressure set solubility limits and partition coefficients. Therefore, models should be at least temperature sensitive. Moreover, since contaminants have different solubility in water, a single water-using operation may need to respond to different models, one for each type of pollutant. This fact adds a new dimension of complexity to an already difficult multi-contaminant problem. Some of these issues are slowly surfacing in the literature. For example, Huang et al. (1999) already refer to the constant concentration in the outlet of some water using processes as well as treatment units.

6.2. Retrofit of existing plants

This problem needs to be focused differently than the design problem. As mentioned before, water reuse may be limited by geographical, process and/ or design constraints. Geographical constraints relate to actual distances or interconnection limitations among units and become of importance when retrofitting existing sites. In such cases, connections may need to be imposed (compulsory connections) or forbidden. The optimal reuse may demand connections that are technically impossible to fulfill. Consequently, full water reuse may be reduced, forcing an increase in fresh water usage. Design constraints deal with issues such as vessel, pipe lines and pumps/compressors capacities as well as with corrosion limitations. For instance, replacing fresh water with reusable wastewater usually implies an increase in flow rates and/or residence times. Such increase may not be feasible for existing equipment. Vessels and piping may to admit wastewater where corrosion limits exceed the original design allowances. The optimal water reuse scheme needs now to include other important variables such as re-piping and new pumping cost. Therefore, the objective may now depart from the minimization of fresh water consumption to include the aforementioned costs. Even though, retrofit options have been mentioned in several papers, (Alva-Argáez et al., 1999; Huang et al., 1999), pumping costs have not been included and heat integration is absent. One attempt to address the problem directly has been recently done by Bagajewicz, Savelski and Rodera (1999b) and Bagajewicz et al. (2000b). The burning challenge in

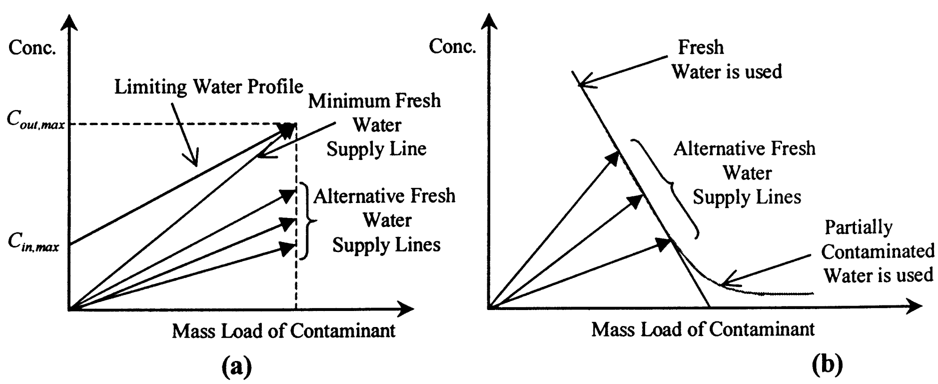

Fig. 25. Concentration–load diagrams.

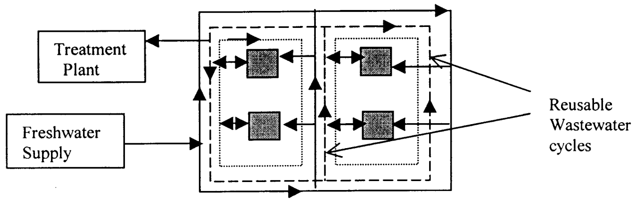

Fig. 26. The water belt.

these systems is the large number of integers that these MINLP models can have, which can induce a cumbersome integrality gap.

6.3. Water belt

This is a new concept that has been suggested as a model to incorporate realistically plant layout consideration to this problem. In this model, two sets of piping cruise an entire battery running along all water-using units. One pipe transports make-up fresh water while the second pipe(s) collects wastewater from the processes and delivers reusable wastewater at the same time. To avoid excessive wastewater degradation, the second pipe may actually be a bundle running together and selectively receiving and discharging wastewater as needed. Fig. 26 illustrates the concept of the water belt in a simplified diagram. Two processes are shown receiving fresh water and wastewater from headers and discharging it in the wastewater header. Such design presents a step ahead towards a zero discharge cycle achievement and breaks with the traditional process-to-process representation of this problem showing that significant savings in piping can be obtained.

6.4. Uncertainty and flexibility of contaminant loads

Wastewater flow rate as well as contaminant levels can vary. Especially in refineries, crudes carry more heavy hydrocarbons than others, and even the amount of aromatic and naphtenic components changes among crudes. Heavy crudes (low API gravity) have a larger proportion of heavier hydrocarbons and therefore the TBP curve is steep. This suggests that the design attempted should be resilient and able to accommodate different pollutant levels.

Resiliency and flexibility have been addressed by several authors in the context of particular applications such as heat exchangers (Colberg, Morari & Townsend, 1978; Floudas & Grossmann, 1987). Some authors have addressed the overall plant resiliency problem (Morari, 1983). Recently, the problem has been initiated as part of what is called 'design with uncertainties'. Straub and Grossmann (1993) and Pistikopoulos and Ierapetritou (1995) are some of the pioneering papers in the area. Many others follow.

6.5. Heat integration

Even though a significant step in the direction of heat integration has been made, there are still some unresolved matters. Systems like those shown in Fig. 21 cannot be obtained automatically. A model accounting for the splitting of the fresh water stream and/or the merging of the wastewater streams is needed.

6.6. Use of mass exchanger network (MEN) technology

Even though an early paper on MEN technology addresses directly the removal of phenol from wastewater streams, this tool has not been exploited to its full extent. Unfortunately, pinch operators for multicomponent systems are not easy to build, and the use of recent novel ideas might be necessary (IDEAS; Drake and Manousiouthakis, 1998).

7. Conclusions

After the seminal paper by Takama et al. (1980), water management in process plants has grown from a humble start in the early nineties to a mature field where complex situations are analyzed and solved. Throughout the years, the field has evolved from being dominated by the use of conceptual design procedures to the current almost exclusive use of mathematical programming. This paper has reviewed several of these advances. Practical numerical challenges are still apparent. Some conceptual challenges remain defiant.

8. Nomenclature

C_{out}	concentration at the outlet of process i
C_{out}^{max}	maximum concentration at the outlet of process i
C_{in}	concentration at the inlet of process i
C_{in}^{max}	maximum concentration at the inlet of process i
F_j^w	flow rate of fresh water to process i
$F_{i,j}$	flow rate of wastewater from process i to process j
H	set of head processes
$L_{k,i}$	contaminant load of pollutant k in process i
$\boldsymbol{P}_j$	set of precursor processes of process j
$\boldsymbol{R}_j$	set of receiver processes from process j
$Y_{i,j}$	binary variable indicating whether there is flow from process i to process j

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