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On the optimality conditions of water utilization systems in process plants with single contaminants

Mariano J. Savelski[1], Miguel J. Bagajewicz*

School of Chemical Engineering and Materials Science, University of Oklahoma, 100 E Body, T-335, Norman, OK 73019-0628, USA

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Abstract

This paper introduces necessary conditions of optimality for water-using networks in refineries and process plants. These necessary conditions correspond to the optimal water allocation planning (WAP) problem that considers wastewater reuse on the basis of a single contaminant and where the objective is to minimize the total water intake. The conditions under which degenerate solutions are possible are also identified. Examples are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Water systems; Wastewater minimization; Reuse; Recycle; Regeneration

1. Introduction

The petroleum refineries as well as the chemical and petrochemical industry make an intensive usage of water. As a result, wastewater streams containing several contaminants (phenols, sulfides, ammonia, benzene, oil, etc.) create an environmental pollution problem. Water cleanup has been the object of several retrofit programs in industry, and legislation exist that regulate and establish goals for these efforts (e.g. Clean Water Act in the USA).

Wastewater has several contaminants that make it unsuitable 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 EPA Clean Water Act of 1977, wastewater must be treated 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.*

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 even more. Regardless of the treatment level, the unit operations for wastewater treatment are classified as physical, chemical, thermal, and biological.

For decades, the primary concern has always focused on end-of-pipe wastewater treatment. End-of-pipe solutions have been seen as the sole remedy to meet the imposed discharge limits. Scarcity of water, rising energy costs and stricter regulations on industrial effluents have created a new and different view on water usage. When pollutants are selectively removed during the process, the wastewater can be reused and/or recycled. This produces a direct impact in the overall amount of fresh makeup water usage as well as in the amount of wastewater that reaches final treatment. Afterwards, the main concern shifted towards solutions that maximize water reuse. Zero water discharge cycles became a desired goal for grassroots design or retrofit. The concept of zero discharge, although plausible, politically

[1] Present address: Rowan University.

* Corresponding author. Tel.: + 1-405-325-5458; fax: + 1-405-325-5813.

E-mail addresses: savelski@rowan.edu (M. J. Savelski), bagajewicz@ou.edu (M. J. Bagajewicz).

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correct and environmentally sound, may come at the expenses of additional capital expenditure. Therefore, as tradeoffs are present, it is a matter that should be further investigated.

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

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 USA Environmental Protection Agency (EPA) Risk Reduction Engineering Laboratory. However, for many processes the reduction of the generation of many 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.

In addition to the improved efficiency obtained by analyzing wastewater treatment facilities and reducing the sources of pollutants, the concept of reusing water started to be investigated systematically in the eighties. This problem has received the name of Water/Wastewater Allocation Planning (WAP) problem. The search for optimal wastewater reuse solutions was addressed by industry itself more than twenty years ago (Carnes, Ford & Brady, 1973; Skylov & Stenzel, 1974; Hospondarec & Thompson, 1974; Mishra, Fan & Erickson, 1975). Two major systematic strategies were developed: The use of superstructures coupled with mathematical programming and a graphic targeting procedure coupled with loop breaking.

Takama, Kuriyama, Shiroko and Umeda (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.

Wang and Smith (1994) presented a method for single contaminants based on targeting. In the same paper a procedure for multiple contaminants is attempted. The basic concept underlying the methodology is mass exchanger network (MEN) technology, which was in turn first proposed by El-Halwagi and Manousiouthakis (1989) and was applied to the removal of phenol from refinery wastewater (El-Halwagi & Manousiouthakis, 1990). Wang and Smith (1994) also explored options of regenerating wastewater even when the pollutant level has not reach end-of-pipe conditions, or has not be reused throughout the entire process. Dhole, Ramchandhani, Tainsh and Wasilewski (1996) popularized this methodology calling it the "water pinch".

The "water pinch" approaches the WAP using targeting graphical representations and techniques on superstructures of alternative designs. The targeting graphical method exploits the idea of plotting the cumulative exchanged mass vs. composition for a set of rich and lean streams, a concept first presented by El-Halwagi and Manousiouthakis (1989) for synthesizing Mass Exchanger Networks. In the "water pinch", this concept is modified to plot mass loads vs. concentration. The limiting water profile line drawn in a concentration vs. mass transferred plot represents every water-using unit. To construct this profile, each process is modeled by a line that starts and ends on imposed maximum inlet and outlet concentrations, respectively. Once all units are accounted for, a combined composite curve from all limiting profiles is created. This composite curve represents the overall behavior of the system as a single water-using unit. A fresh water supply line is then matched against the composite curve to reach a pinch point other than the origin. This supply line is the counterpart of the composite lean stream in a Mass Exchanger Network (El-Halwagi & Manousiouthakis, 1989). Thus, even though there is the impression that this is a separate area of research, this is in reality a special case of mass exchanger networks.

The inverse of the slope of the water supply line will render a flowrate. The minimum possible water flowrate is guaranteed by maximizing the slope up to the pinch point. The single contaminant water composite curve is fairly easy to obtain. Once the target flowrate is obtained the authors proposed a matching method similar to the procedure followed when constructing Heat Exchanger Networks (Linhoff & Hindmarsh, 1983). Finally, the loops created by the matching procedure are removed to render a realistic network of the water-using operations. These procedures have some difficulties:

- Simplification of the preliminary designs involves loops identification and then breaking with the goal of having one match per process. At this step, Wang and Smith (1994) utilize the same relaxation method introduced by Linhoff and Hindmarsh (1983) for the design of heat exchanger networks. Loops are easy to identify and break in small problems. However, when the problem becomes larger and the loops overlap, the sequence of loop breaking is not at all clear.
- Even after simplifying the network by loop breaking, the proposed design may require unrealistic splitting of unit operations. This is a result of the inability of the method to break all the loops.

Olesen and Polley (1997) recognize the difficulties of the design procedure proposed by Wang and Smith (1994) and introduced a simplified design procedure for single contaminant. The authors use the water-pinch to obtain the target minimum flowrate and then model the realizing network by inspection. However, this approach cannot handle more than four or five operations as stated by the authors, because it is based on a special ad-hoc inspection procedure.

On the other hand, the use of superstructures presents several numerical limitations. For example, before solving, Takama et al. (1980) transformed the model into a series of problems without inequality constraints by using a penalty function and finally solving it using the Complex method.

All superstructure models require large number of constraints to mathematically represent the component and overall mass balances. Due to the nonlinear nature of these constraints the straight use of NLP packages to solve the problem often renders infeasible solutions. Therefore, relaxation techniques need to be applied to first solve the problem and get feasible starting points for the NLP problem. Even after the problem has been successfully solved there is no guarantee over the optimality of the optimum.

In this paper we present *necessary conditions of optimality* for the *single-contaminant* WAP problem, as it has been posed by Wang and Smith (1994). These conditions will be used as part of a design procedure for the WAP problem, which will be presented in future papers. The Problem statement is given first. The necessary conditions are one by one proved in a series of theorems. Some comments are included in the text, but complete examples are analyzed out in a separate section.

2. Problem statement

Given a set of water-using/water-disposing processes, it is desired to determine a network of interconnections of water streams among the processes so that the overall fresh water consumption is minimized while the processes receive water of adequate quality. This is what is referred to as the Water/Wastewater Allocation Planning (WAP) problem.

A more stringent version of this problem was presented by Takama, et al. (1980) and later used by Wang and Smith (1994). In this version, limits on inlet and an outlet concentration of pollutant are imposed a priori on each process and a fixed load of contaminants is used. These inlet and outlet concentrations limits account for corrosion, fouling, maximum solubility, etc.

Before we discuss our necessary conditions of optimality, some definitions that will be useful later are presented.

3. Definitions

The following types of water-using sets and processes can be defined:

Fresh Water User (*FWU*) *processes*: Fresh water user processes are processes that require fresh water. They may also be consumers of wastewater.

Wastewater User (*WWU*) *processes*: Wastewater user processes are processes that are fed solely by wastewater.

Head (*H*) *processes*: Head process is a special case of a FWU that utilizes only fresh water.

Intermediate (*I*) *wastewater user processes*: Intermediate wastewater user processes are processes that are fed by wastewater from other processes and feed other processes with the wastewater they produce.

Terminal (*T*) *wastewater user processes*: Terminal wastewater user processes are processes that are fed by wastewater from other processes, but they discharge their wastewater to treatment.

Fig. 1 illustrates schematically the way these processes are aligned. The set of fresh water users consists of the set H and subsets of sets I and T. Similarly, the set of wastewater users is formed by a subset of I and a subset of T. That is, not all intermediate and terminal processes use fresh water and/or are solely fed by wastewater.

We now define the concept of a *set of precursors* and a *set of receivers*.

Set of precursors (P_j) *of a process j*: A set of *precursors* of a process is the set of all processes that send wastewater to process j.

Set of receivers (R_j) *of process j*: A set of *receivers* of a process is the set of all processes where wastewater from process j is sent.

Finally, the following definitions will help in the presentation of the necessary conditions.

Partial wastewater providers (*PWP*): A *partial wastewater provider* is a process whose wastewater is partially reused by other processes, that is, a portion of its wastewater is sent directly to treatment.

Total wastewater providers (*TWP*): A *total wastewater provider* is a process whose wastewater is fully reused by other processes.

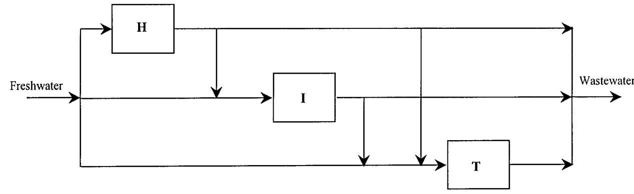

Fig. 1. Schematic representation of a water network.

4. Necessary conditions of optimality

The necessary conditions of optimality are presented in a sequence of theorems.

Theorem 1 (Necessary condition of concentration monotonicity). *If a solution to the WAP is optimal, then at every Partial Wastewater Provider (PWP), 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 that satisfies the definition of PWP, that is $F_{j,\text{out}} > 0$, *then* $C_{j,\text{out}} \geqslant C_{P_j,j}$, *where* $C_{P_j,j}$ *is the concentration of the combined wastewater of all the precursors.*

Fig. 2 presents the set of interconnections of interest, omitting other existing ones that are not of relevance to this case.

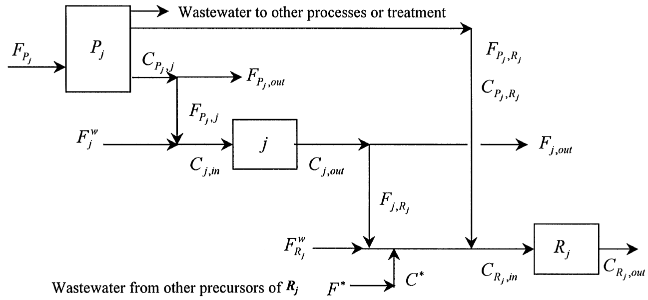

Fig. 2. Precursors and receivers of process *j*.

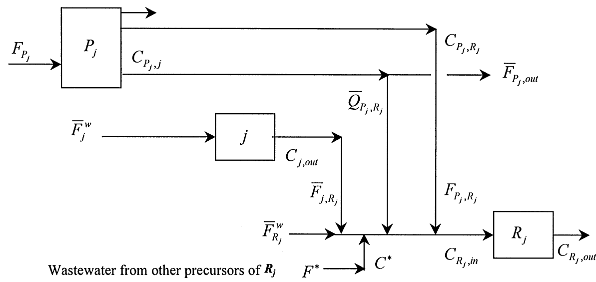

Fig. 3. Restoring downstream feasibility.

Proof. The proof is by contradiction: Assume that $C_{P_j,j} > C_{j,\text{out}}$. A component mass balance over process j is:

$$F_{P_j,j}C_{P_j,j} + L_j = (F_{P_j,j} + F_j^w)C_{j,\text{out}} \tag{1}$$

where L_j is the load of process *j*. Rewriting Eq. (1),

$$F_j^w = \frac{L_j}{C_{j,\text{out}}} + \left(\frac{C_{P_j,j}}{C_{j,\text{out}}} - 1\right)F_{P_j,j}. \tag{2}$$

But, by assumption

$$\left(\frac{C_{P_j,j}}{C_{j,\text{out}}} - 1\right) > 0. \tag{3}$$

Thus, if $F_{P_j,j}$ (which is positive) is reduced to zero a new fresh water flowrate, $\bar{F}_j^w = L_j/C_{j,\text{out}} < F_j^w$ is obtained, contradicting the hypothesis that the original structure is optimal. To complete the proof one only needs to show that such reduction can be performed without altering any conditions downstream.

Two cases are possible:

(a) Process *j* can still supply all the necessary wastewater to the set R_j, that is, $\bar{F}_j^w \geqslant F_{j,R_j}$. In this case, since no flowrate or concentration perturbation takes place downstream from process *j*, the theorem is proved.
(b) Process *j* cannot deliver the same amount of wastewater to the set R_j, that is, $\bar{F}_j^w < F_{j,R_j}$. Thus, feasibility conditions downstream of process *j* need to be restored.

Since it has been proven that the fresh water consumption of process *j* can be reduced to its minimum by eliminating $F_{P_j,j}$, downstream feasibility may be restored by reusing part or all this available wastewater. Fig. 3 shows the new situation.

We will now show that:

(b.1) Feasibility can be restored by reusing a flowrate $\bar{Q}_{P_j,R_j}$ which has the same concentration $C_{P_j,j}$.
(b.2) The new flowrate $\bar{Q}_{P_j,R_j}$ does not exceed the previous value used $F_{P_j,j}$. That is $\bar{Q}_{P_j,R_j} \ni (0, F_{P_j,j}]$.
(b.3) In this new scheme of flowrates, the overall fresh water intake goes down ($\Delta W < 0$).

(b.1) Since $\bar{F}_j^w < F_{j,R_j}$, all the wastewater available from process *j* can now be sent to the set R_j, resulting in

$$\bar{F}_j^w = \bar{F}_{j,R_j}. \tag{4}$$

The conditions downstream are not altered only if $C_{R_j,\text{in}}$ and the total flowrate feeding the set R_j do not change. Since now process *j* cannot satisfy the demand, the precursor set P_j can be used as a source of wastewater. The amount needed should satisfy:

$$C_{R_j,\text{in}} = \frac{F_{j,R_j}C_{j,\text{out}} + F_{P_j,R_j}C_{P_j,R_j} + F^*C^*}{F_{j,R_j} + F_{P_j,R_j} + F_{R_j}^w + F^*}$$
$$= \frac{\bar{F}_{j,R_j}C_{j,\text{out}} + \bar{Q}_{P_j,R_j}C_{P_j,j} + F_{P_j,R_j}C_{P_j,R_j} + F^*C^*}{\bar{F}_{j,R_j} + \bar{Q}_{P_j,R_j} + F_{P_j,R_j} + \bar{F}_{R_j}^w + F^*}, \tag{5}$$

$$F_{j,R_j} + F_{P_j,R_j} + F_{R_j}^w + F^* = \bar{F}_{j,R_j} + \bar{Q}_{P_j,R_j} + F_{P_j,R_j} + \bar{F}_{R_j}^w + F^*. \tag{6}$$

Using Eq. (6) to cancel the denominators in both sides of Eq. (5) and rearranging, we obtain

$$\bar{Q}_{P_j,R_j} = \frac{C_{j,\text{out}}}{C_{P_j,j}} F_{j,R_j} - \frac{C_{j,\text{out}}}{C_{P_j,j}} \bar{F}_{j,R_j} = \frac{F_{j,R_j} - \bar{F}_{j,R_j}}{\alpha} \tag{7}$$

where $\alpha = C_{P_j,j}/C_{j,\text{out}}$.

(b.2) We now prove that the new wastewater flowrate $\bar{Q}_{P_j,R_j}$ to the set of processes is feasible. Since we have established that downstream conditions are maintained unaltered by keeping inlet conditions at the set R_j, unchanged, then the total component flow, $f_{R_j,\text{in}}$, that the set R_j, is receiving before and after reducing F_j^w to $\bar{F}_j^w$ remains constant as well.

Therefore we can write

$$\begin{aligned} f_{R_j,\text{in}} &= f_{j,R_j} + f_{P_j,R_j} + F^*C^* \\ &= \bar{f}_{j,R_j} + f_{P_j,R_j} + \bar{q}_{P_j,R_j} + F^*C^*. \end{aligned} \tag{8}$$

But since $\bar{f}_{j,R_j} = L_j$, because only fresh water is now sent to process j, then, after simplifying, we get

$$f_{j,R_j} = L_j + \bar{q}_{P_j,R_j}. \tag{9}$$

Besides,

$$f_{P_j,j} + L_j \geqslant f_{j,R_j} \tag{10}$$

because $F_{j,\text{out}} \geqslant 0$. Replacing Eq. (9) in Eq. (10) we get

$$f_{P_j,j} + L_j \geqslant \bar{q}_{P_j,R_j} + L_j. \tag{11}$$

After canceling L_j from both sides of Eq. (11) and replacing the component flows by their definitions, we obtain

$$F_{P_j,j} C_{P_j,j} \geqslant \bar{Q}_{P_j,R_j} C_{P_j,j}. \tag{12}$$

Consequently,

$$F_{P_j,j} \geqslant \bar{Q}_{P_j,R_j}. \tag{13}$$

(b.3) We now prove that the total water intake is lower. The change in water intake is:

$$\Delta W = \Delta F_{P_j}^w + \Delta F_j^w + \Delta F_{R_j}^w \tag{14}$$

where $\Delta F_i^w = \bar{F}_i^w - F_i^w$. Replacing $\bar{Q}_{P_j,R_j}$ obtained from Eq. (6) in Eq. (7) and rearranging,

$$\bar{F}_{R_j}^w - F_{R_j}^w = \left(1 - \frac{1}{\alpha}\right)(F_{j,R_j} - \bar{F}_{j,R_j}). \tag{15}$$

Thus, recalling that $\Delta F_{P_j}^w = 0$, and $\Delta F_j^w = (1-\alpha)F_{P_j,j}$, which can be obtained from Eq. (2), Eq. (14) becomes

$$\Delta W = (1-\alpha)F_{P_j,j} - \left(1 - \frac{1}{\alpha}\right)(\bar{F}_{j,R_j} - F_{j,R_j}). \tag{16}$$

Rearranging

$$\Delta W = (1-\alpha)\left(F_{P_j,j} + \frac{\bar{F}_{j,R_j} - F_{j,R_j}}{\alpha}\right). \tag{17}$$

But

$$\bar{F}_{j,R_j} = \bar{F}_j^w = F_j^w - \Delta F_{P_j,j} = F_j^w - (\alpha - 1)F_{P_j,j}. \tag{18}$$

In turn, using a balance around process j to obtain F_j^w, Eq. (18) can be rewritten as follows:

$$\bar{F}_{j,R_j} = F_{j,R_j} + F_{j,\text{out}} - \alpha F_{P_j,j}. \tag{19}$$

Replacing Eq. (19) in Eq. (17) and in virtue that $F_{j,\text{out}} > 0$, we obtain

$$\Delta W = (1-\alpha)\frac{F_{j,\text{out}}}{\alpha} < 0. \qquad \square \tag{20}$$

Corollary 1. *If for a given process j a solution is optimal and $C_{P_j,j} = C_{j,\text{out}}$, then the solution is degenerated in the sense that any wastewater sent to process j from its precursors does not alter the total water intake.*

Proof. When $C_{P_j,j} = C_{j,\text{out}}$, Eq. (2) states that $L_j = F_j^w C_{j,\text{out}}$. That is the interconnection between the set P_j and process j is of no practical use when seeking a decrease in F_j^w. $\square$

A practical consequence of this corollary is that any optimal design can have different flowrates going through process j. In particular $F_{P_j,j}$ can have any value in the interval $[0, \tilde{F}_{P_j,j}]$ where $\tilde{F}_{P_j,j}$ is the maximum flowrate that process j can admit without violating the inlet concentration constraint. This flowrate $\tilde{F}_{P_j,j}$ is such that the inlet concentration of process j reaches its maximum and can be found as follows:

Perform a component mass balance over process j at the inlet:

$$\tilde{F}_{P_j,j} C_{P_j,j} = (\tilde{F}_{P_j,j} + F_j^w) C_{j,\text{in}}^{\max}. \tag{21}$$

Rearranging,

$$\tilde{F}_{P_j,j} = \frac{F_j^w}{\left(\dfrac{C_{P_j,j}}{C_{j,\text{in}}^{\max}} - 1\right)}. \tag{22}$$

As long as $F_{P_j} \leqslant \tilde{F}_{P_j,j}$, then $C_{j,\text{in}} \leqslant C_{j,\text{in}}^{\max}$. Repeating Eq. (21) for generic inlet conditions, we get

$$F_{P_j,j} C_{P_j,j} = (F_{P_j,j} + F_j^w) C_{j,\text{in}} \tag{23}$$

or after rearranging

$$F_{P_j,j} = \frac{F_j^w}{\left(\dfrac{C_{P_j,j}}{C_{j,\text{in}}} - 1\right)}. \tag{24}$$

Since $F_{P_j} \leqslant \tilde{F}_{P_j,j}$, using Eqs. (22) and (24) it is easy to see that $C_{j,\text{in}} \leqslant C_{j,\text{in}}^{\max}$. The calculations can be repeated for any other subset of precursors.

Thus, taking a decision on whether to send wastewater through process j or not depends upon the project scope. If designing a new facility one may want to minimize the intake of a particular piece of equipment to reduce its cost if this cost is mostly based on the volume the equipment handles, i.e. a flash tank. But if the equipment size

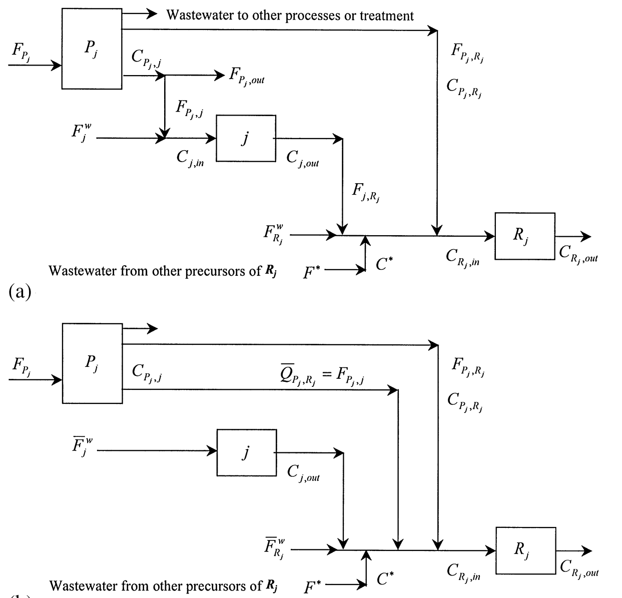

Fig. 4. (a). Process j as a TWP. (b). Monotonicity restoration.

highly depends on separation efficiency, i.e. a stripping column, then a lower inlet concentration could be beneficial and overcome any extra expenditure due to volume over sizing. Another consideration is the number of interconnection and flow controls required when dealing with multiple feeds. Obviously, there exists a trade-off and an optimum situation could lie in an intermediate flowrate, $F_{P_j,j} \ni [0, \tilde{F}_{P_j,j}]$. In retrofitting, possibilities may be more stringent because the equipment already exists.

Corollary 2. *If a process is a TWP there exist at least one possible optimal solution that satisfies monotonicity.*

Proof. Consider Fig. 4(a) where it has been assumed that process j is a TWP ($F_{j,\text{out}} = 0$) and Fig. 4(b) that shows a proposed alternative solution. Basically, this alternative solution consists of eliminating the stream of wastewater that is being sent to process j from its precursors, as this is the connection that breaks monotonicity. A new connection is added where part (or all) the wastewater formerly sent to process j is now sent to its receivers. From (b.1) and (b.2) (Theorem 1) there exist a $\bar{Q}_{P_j,R_j}$ with concentration $C_{P_j,j}$ that can be sent to the set R_j while maintaining feasibility. In addition, it was proved that $\bar{Q}_{P_j,R_j} \ni (0, F_{P_j,j}]$.

We now determine $\bar{Q}_{P_j,R_j}$. Since the total flowrate at the inlet of the set R_j stays constant, equate the total flowrate at inlet R_j before and after monotonicity restoration, that is:

$$F_{P_j,j} + F_j^w + F_{R_j}^w + F_{P_j,R_j} + F^* = \bar{F}_j^w + \bar{F}_{R_j}^w + F_{P_j,R_j} + F^* + \bar{Q}_{P_j,R_j}. \quad (25)$$

After canceling common terms and rearranging, we obtain

$$F_{P_j,j} = [(\bar{F}_j^w - F_j^w) + (\bar{F}_{R_j}^w - F_{R_j}^w)] + \bar{Q}_{P_j,R_j}. \quad (26)$$

By definition of ΔW:

$$F_{P_j,j} = \Delta W + \bar{Q}_{P_j,R_j}. \quad (27)$$

From Eq. (20), $\Delta W = 0$ then $\bar{Q}_{P_j,R_j} = F_{P_j,j}$. In conclusion, we have proven that by making $\bar{Q}_{P_j,R_j} = F_{P_j,j}$ the alternative solution is not only optimal but also monotone. □

4.1. Necessary condition of maximum outlet concentration

We will now prove that if a solution of the WAP problem is optimal then all FWU processes have reached their maximum possible outlet concentration. A second possibility is that they constitute a degenerate solution for which an equivalent one with the concentration at its maximum exists.

Three theorems, each corresponding to a different type of FWU process, are used to prove this necessary condition.

Theorem 2 (Necessary condition of maximum concentration for head processes). *If a solution of the WAP problem is optimal, then the outlet concentration of a Head Process is equal to its maximum or an equivalent solution with the same overall freshwater consumption exists in which the concentration is at its maximum.*

Proof. We will prove the theorem by contradiction: Consider a head process h. Assume $C_{h,\text{out}} < C_{h,\text{out}}^{\max}$. Then, since the load L_h is constant we have

$$L_h = F_h^w C_{h,\text{out}} = \bar{F}_h^w C_{h,\text{out}}^{\max} \quad (28)$$

where $\bar{F}_h^w$ is the flowrate of water corresponding to the $C_{h,\text{out}}^{\max}$. Therefore

$$\bar{F}_h^w = \frac{C_{h,\text{out}}}{C_{h,\text{out}}^{\max}} F_h^w < F_h^w. \quad (29)$$

Thus, the water intake can be reduced in the case where water is not reused.

In the case where the water is reused downstream, Eq. (29) still constitutes a proof if one is able to show that after the reduction, the conditions downstream remain feasible. Fig. 5 shows downstream reuse of a head process wastewater outlet. For this purpose, consider the flowrate F_{h,R_h} from process h to a set of its receivers. Assume that these flowrates and the corresponding fresh water intake flowrates $F_{R_h}^w$ are changed so that the concentrations $C_{R_h,\text{in}}$ and the incoming flowrate to the set R_h remain constant.

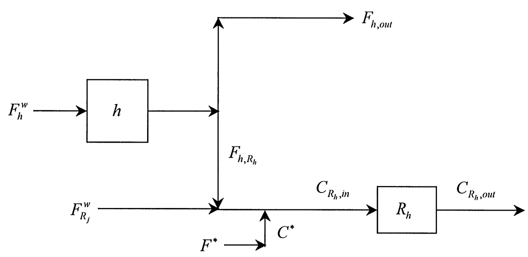

Fig. 5. A head process and its receivers.

The original and new sets need to satisfy the following relations:

$$F_{h,R_h} C_{h,\text{out}} + F^* C^* = C_{R_h,\text{in}}(F_{h,R_h} + F^w_{R_h} + F^*), \tag{30}$$

$$\bar{F}_{h,R_h} C^{\max}_{h,\text{out}} + F^* C^* = C_{R_h,\text{in}}(\bar{F}_{h,R_h} + \bar{F}^w_{R_h} + F^*), \tag{31}$$

$$F_{h,R_h} + F^w_{R_h} + F^* = \bar{F}_{h,R_h} + \bar{F}^w_{R_h} + F^*. \tag{32}$$

From Eq. (29) one obtains

$$\bar{F}^w_h - F^w_h = -(1-\beta) F^w_h \tag{33}$$

where $\beta = C_{h,\text{out}}/C^{\max}_{h,\text{out}}$. Dividing Eq. (31) by Eq. (30) and using Eq. (32) one also obtains

$$\bar{F}_{h,R_h} = \beta F_{h,R_h}. \tag{34}$$

We now substitute Eqs. (29) and (31) in the definition of $\bar{F}_{h,\text{out}}$, as follows:

$$\bar{F}_{h,\text{out}} = \bar{F}^w_h - \bar{F}_{h,R_h} = \beta(F^w_h - F_{h,R_h}) = \beta F_{h,\text{out}} \tag{35}$$

from which we conclude that the new water consumption pattern is feasible. Substituting Eq. (34) into Eq. (32) and rearranging,

$$\bar{F}^w_{R_h} - F^w_{R_h} = (1-\beta) F_{h,R_h}. \tag{36}$$

The total difference in fresh water flowrate between the proposed solution and the new one is

$$\Delta W = (\bar{F}^w_h - F^w_h) + (\bar{F}^w_{R_h} - F^w_{R_h}). \tag{37}$$

Substituting Eqs. (33) and (36) into Eq. (37),

$$\begin{aligned}\Delta W &= -(1-\beta) F^w_h + (1-\beta) F_{h,R_h} \\ &= (1-\beta)(F_{h,R_h} - F^w_h).\end{aligned} \tag{38}$$

Since

$$F_{h,R_h} - F^w_h = -F_{h,\text{out}} \leqslant 0. \tag{39}$$

Then

$$\Delta W = -(1-\beta) F_{h,\text{out}}. \tag{40}$$

When $F_{h,\text{out}} \neq 0$, then $\Delta W < 0$ (because $\beta < 1$), which contradicts the assumption of optimality. When $F_{h,\text{out}} = 0$, by Eq. (40) we have $\Delta W = 0$. This means that a degenerated solution has been found. This solution is equivalent to one with the concentration at its maximum. □

Theorem 3 (Necessary condition of maximum concentration for intermediate processes)**.** *If the solution of the WAP problem is optimal then the outlet concentration of an Intermediate Process reaches its maximum or an equivalent solution with the same overall freshwater consumption exists where the concentration is at its maximum.*

Proof. Assume that neither $C_{j,\text{in}}$ nor $C_{j,\text{out}}$ are at their maximum possible values, that is $C_{j,\text{in}} < C^{\max}_{j,\text{in}}$ and $C_{j,\text{out}} < C^{\max}_{j,\text{out}}$.

Consider the set of processes P_j. These processes are precursors of j, but they are also precursors of R_j and other processes. We define $\hat{F}_{P_j}$ as the sum of the water sent to j, plus the portion sent to treatment, that is $\hat{F}_{P_j} = F_{P_j,\text{out}} + F_{P_j,j}$. Consider using thus total flowrate as feed to process j. Consider at the same time an adjustment of the fresh water sent to process j so that the outlet concentration remains the same. To do this, assume a new inlet concentration for process j. Then, the following holds:

$$\hat{C}_{j,\text{in}} = \frac{\hat{F}_{P_j} C_{P_j,j}}{\hat{F}_{P_j} + \hat{F}^w_j}, \tag{41}$$

$$L_j = (\hat{F}_{P_j} + \hat{F}^w_j)(C_{j,\text{out}} - \hat{C}_{j,\text{in}}). \tag{42}$$

We recognize two conditions, *Case* I: $\hat{C}_{j,\text{in}} \geqslant C^{\max}_{j,\text{in}}$ and *Case* II: $\hat{C}_{j,\text{in}} < C^{\max}_{j,\text{in}}$.

The outline of the proof is as follows. We first show that an increase in the flowrate from the precursors (P_j) of process j reduces the total water intake of process j. As a result, either the maximum inlet concentration is reached (Case I), or all the water from the precursors is used up (Case II). A condition is imposed in this reduction so that the outlet concentration of process j remains constant. This reduction, does not alter conditions downstream at the inlet of the receivers of process $j(R_j)$. We now outline the proof for each case separately.

Case I: $\hat{C}_{j,\text{in}} \geqslant C^{\max}_{j,\text{in}}$. In this case, we will prove the theorem by first proving that the inlet concentration of process j can be made equal to its maximum, with a reduction of the water intake of process j. Finally we will show that the total fresh water intake of the system can be lowered by maximizing the outlet concentration of process j.

Case II: $\hat{C}_{j,\text{in}} < C^{\max}_{j,\text{in}}$. In this case, we will prove that the outlet concentration of process j can be made equal to its maximum, with a reduction of the total water intake.

Case I (*Inlet concentration binding condition*). In this case, starting from Eq. (42)

$$L_j = (\hat{F}_{P_j} + \hat{F}^w_j)(C_{j,\text{out}} - \hat{C}_{j,\text{in}})$$
$$\leqslant (\hat{F}_{P_j,j} + \hat{F}^w_j)(C_{j,\text{out}} - C^{\max}_{j,\text{in}})$$
$$= \frac{\hat{F}_{P_j,j} C_{P_j,j}}{\hat{C}_{j,\text{in}}}(C_{j,\text{out}} - C^{\max}_{j,\text{in}})$$
$$\leqslant \frac{\hat{F}_{P_j,j} C_{P_j,j}}{C^{\max}_{j,\text{in}}}(C_{j,\text{out}} - C^{\max}_{j,\text{in}}). \tag{43}$$

Therefore

$$\left(\frac{C_{j,\text{out}}}{C^{\max}_{j,\text{in}}} - 1\right) \geqslant \frac{L_j}{\hat{F}_{P_j} C_{P_j,j}} \tag{44}$$

which is an inequality that will be useful later.

We will prove that the water consumption can be reduced by increasing $F_{P_j,j}$ until the maximum inlet concentration is reached, while maintaining $C_{j,\text{out}}$ constant.

Since

$$C_{j,\text{in}} < C^{\max}_{j,\text{in}} \tag{45}$$

then an increase in $F_{P_j,j}$ will increase $C_{j,\text{in}}$. Now $F_{P_j,\text{out}} > 0$, otherwise, by Eq. (44) the inlet concentration to process j would be violating the constraint. Therefore the increase in $F_{P_j,j}$ is feasible. Let the new flowrates be $\bar{F}_{P_j,j}$ and $\bar{F}^w_j$.

From a balance in the inlet node, we obtain

$$C^{\max}_{j,\text{in}} = \frac{\bar{F}_{P_j,j} C_{P_j,j}}{\bar{F}_{P_j,j} + \bar{F}^w_j}. \tag{46}$$

In addition a component balance on process j gives

$$C_{j,\text{out}} = \frac{\bar{F}_{P_j,j} C_{P_j,j} + L_j}{\bar{F}_{P_j,j} + \bar{F}^w_j}. \tag{47}$$

Divide Eq. (47) by Eq. (46)

$$\frac{C_{j,\text{out}}}{C^{\max}_{j,\text{in}}} = \frac{\bar{F}_{P_j,j} C_{P_j,j} + L_j}{\bar{F}_{P_j,j} C_{P_j,j}} = \left(1 + \frac{L_j}{\bar{F}_{P_j,j} C_{P_j,j}}\right). \tag{48}$$

Rearranging:

$$\bar{F}_{P_j,j} = \frac{L_j}{C_{P_j,j}} \frac{1}{\left(\dfrac{C_{j,\text{out}}}{C^{\max}_{j,\text{in}}} - 1\right)}. \tag{49}$$

Repeating the same procedure for the original conditions one obtains

$$F_{P_j,j} = \frac{L_j}{C_{P_j,j}} \frac{1}{\left(\dfrac{C_{j,\text{out}}}{C_{j,\text{in}}} - 1\right)} \tag{50}$$

and since $C_{j,\text{in}} < C^{\max}_{j,\text{in}}$, we obtain

$$F_{P_j,j} < \bar{F}_{P_j,j}. \tag{51}$$

Also, rearranging Eq. (47)

$$\bar{F}^w_j = \bar{F}_{P_j,j}\left(\frac{C_{P_j,j}}{C^{\max}_{j,\text{in}}} - 1\right). \tag{52}$$

Similarly

$$F^w_j = F_{P_j,j}\left(\frac{C_{P_j,j}}{C_{j,\text{in}}} - 1\right). \tag{53}$$

Finally, substituting Eq. (49) into Eq. (52) we obtain

$$\bar{F}^w_j = \frac{L_j}{C_{P_j,j}} \frac{\left(\dfrac{C_{P_j,j}}{C^{\max}_{j,\text{in}}} - 1\right)}{\left(\dfrac{C_{j,\text{out}}}{C^{\max}_{j,\text{in}}} - 1\right)}. \tag{54}$$

Similarly, using a set of balances for the assumed optimal condition the following is obtained:

$$F^w_j = \frac{L_j}{C_{P_j,j}} \frac{\left(\dfrac{C_{P_j,j}}{C_{j,\text{in}}} - 1\right)}{\left(\dfrac{C_{j,\text{out}}}{C_{j,\text{in}}} - 1\right)}. \tag{55}$$

We will now prove that $\bar{F}^w_j < F^w_j$ by analyzing the r.h.s. of Eqs. (54) and (55). Multiply both sides of $C_{j,\text{in}} < C^{\max}_{j,\text{in}}$ by $(C_{P_j,j} - C_{j,\text{out}})$,

$$(C_{P_j,j} - C_{j,\text{out}})C_{j,\text{in}} > (C_{P_j,j} - C_{j,\text{out}})C^{\max}_{j,\text{in}}. \tag{56}$$

The sign of the inequality changed as $(C_{P_j,j} - C_{j,\text{out}}) < 0$ by the necessary condition of monotonicity. Rearranging

$$C_{P_j,j}C_{j,\text{in}} + C_{j,\text{out}}C^{\max}_{j,\text{in}} > C_{P_j,j}C^{\max}_{j,\text{in}} + C_{j,\text{out}}C_{j,\text{in}}. \tag{57}$$

Change signs and add $C_{P_j,j}C_{j,\text{out}} + C_{j,\text{in}}C^{\max}_{j,\text{in}}$ to both sides to obtain

$$C_{P_j,j}C_{j,\text{out}} - C_{P_j,j}C_{j,\text{in}} - C_{j,\text{out}}C^{\max}_{j,\text{in}} + C_{j,\text{in}}C^{\max}_{j,\text{in}}$$
$$< C_{P_j,j}C_{j,\text{out}} - C_{P_j,j}C^{\max}_{j,\text{in}} - C_{j,\text{out}}C_{j,\text{in}} + C_{j,\text{in}}C^{\max}_{j,\text{in}}. \tag{58}$$

Further manipulation gives

$$(C_{P_j,j} - C^{\max}_{j,\text{in}})(C_{j,\text{out}} - C_{j,\text{in}})$$
$$< (C_{P_j,j} - C_{j,\text{in}})(C_{j,\text{out}} - C^{\max}_{j,\text{in}}). \tag{59}$$

However $(C_{j,\text{out}} - C^{\max}_{j,\text{in}})$ is positive because of Eq. (44). Then we obtain

$$\frac{(C_{P_j,j} - C^{\max}_{j,\text{in}})}{(C_{j,\text{out}} - C^{\max}_{j,\text{in}})} < \frac{(C_{P_j,j} - C_{j,\text{in}})}{(C_{j,\text{out}} - C_{j,\text{in}})} \tag{60}$$

or

$$\frac{\left(\dfrac{C_{P_j,j}}{C^{\max}_{j,\text{in}}} - 1\right)}{\left(\dfrac{C_{j,\text{out}}}{C^{\max}_{j,\text{in}}} - 1\right)} < \frac{\left(\dfrac{C_{P_j,j}}{C_{j,\text{in}}} - 1\right)}{\left(\dfrac{C_{j,\text{out}}}{C_{j,\text{in}}} - 1\right)}. \tag{61}$$

Using Eq. (61) one can compare Eqs. (54) and (55) and conclude that $\bar{F}_j^w < F_j^w$.

To complete the proof it is necessary to prove that:

(a) $\bar{F}_{P_j,\mathrm{out}} \geqslant 0$, which is part of the assumption made at the beginning of the proof.

(b) $\bar{F}_{j,R_j} = F_{j,R_j}$ is feasible, that is, the conditions downstream do not need to change. In other words, a reduction in fresh water to process j, does not reduce the outlet of this process below what it was sent to its receivers.

Part a ($\bar{F}_{P_j,\mathrm{out}} \geqslant 0$). From Eq. (49)

$$\frac{L_j}{C_{P_j,j}} = \bar{F}_{P_j,j}\left(\frac{C_{j,\mathrm{out}}}{C_{j,\mathrm{in}}^{\max}} - 1\right). \tag{62}$$

Substituting in Eq. (44)

$$\frac{\bar{F}_{P_j,j}}{\hat{F}_{P_j}} \leqslant 1 \tag{63}$$

which completes the proof.

Part b ($\bar{F}_{j,R_j} = F_{j,R_j}$ *is feasible*). A component mass balance over process j reads

$$F_j C_{j,\mathrm{out}} = L_j + F_{P_j,j} C_{P_j,j}, \tag{64}$$

$$\bar{F}_j C_{j,\mathrm{out}} = L_j + \bar{F}_{P_j,j} C_{P_j,j}. \tag{65}$$

Subtracting Eq. (64) from Eq. (65) and dividing by $C_{j,\mathrm{out}}$

$$(\bar{F}_j - F_j) = (\bar{F}_{P_j,j} - F_{P_j,j})\frac{C_{P_j,j}}{C_{j,\mathrm{out}}}. \tag{66}$$

Since $(\bar{F}_{P_j,j} - F_{P_j,j}) > 0$, then $(\bar{F}_j - F_j) > 0$. Therefore, F_{j,R_j} can be always kept constant by increasing $F_{j,\mathrm{out}}$.

To complete the proof we need to show that the maximum outlet concentration of process j can be reached and that this will produce a fresh water intake reduction.

The increase in outlet concentration needs to be accompanied by new conditions to maintain feasibility downstream at the inlet of the receivers from process j. This can be obtained by keeping both $C_{R_j,\mathrm{in}}$ and F_{R_j} constant while proving that there will be sufficient wastewater for reuse, that is $\bar{\bar{F}}_j^w + \bar{\bar{F}}_{P_j,j} \geqslant \bar{\bar{F}}_{j,R_j}$. The fresh water decrease can be achieved by reducing $\bar{F}_{P_j,j}$ and $\bar{F}_j^w$ simultaneously. To guarantee that the overall fresh water consumption will be reduced the excess availability at process j, defined as $(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j})$, will be bypassed to the set R_j. The new situation is shown in Fig. 6.

Now, from Eq. (49) we can write,

$$\bar{\bar{F}}_{P_j,j} = \frac{L_j}{C_{P_j,j}}\frac{1}{\left(\dfrac{C_{j,\mathrm{out}}^{\max}}{C_{j,\mathrm{in}}^{\max}} - 1\right)}. \tag{67}$$

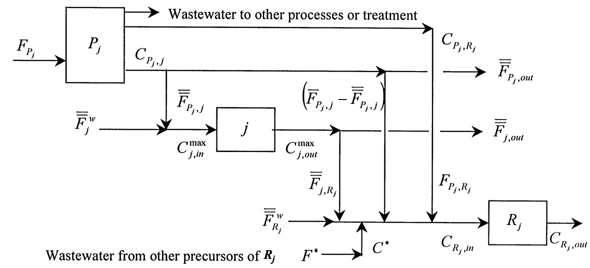

Fig. 6. Optimal water allocation structure.

Comparing Eqs. (49) and (67) it clearly turns out that $\bar{\bar{F}}_{P_j,j} < \bar{F}_{P_j,j}$. The new fresh water supply to process j, $\bar{\bar{F}}_j^w$, can be calculated using Eq. (52), that is:

$$\bar{\bar{F}}_j^w = \bar{\bar{F}}_{P_j,j}\left(\frac{C_{P_j j}}{C_{j,\mathrm{in}}^{\max}} - 1\right) < \bar{F}_j^w. \tag{68}$$

All we need to show now is that these fresh water savings are not overcome by any necessary increased in $F_{R_j}^w$.

Consider a component mass balance of process j at outlet conditions before and after the fresh water reduction.

$$C_{j,\mathrm{out}}(\bar{F}_{P_j,j} + \bar{F}_j^w) = \bar{F}_{P_j,j} C_{P_j,j} + L_j, \tag{69}$$

$$C_{j,\mathrm{out}}^{\max}(\bar{\bar{F}}_{P_j,j} + \bar{\bar{F}}_j^w) = \bar{\bar{F}}_{P_j,j} C_{P_j,j} + L_j. \tag{70}$$

Eliminating L_j from Eqs. (69) and (70), we obtain

$$\bar{\bar{F}}_j^w = \alpha \bar{F}_{P_j,j} + \alpha \bar{F}_j^w - \bar{\bar{F}}_{P_j,j} - \beta(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) \tag{71}$$

where $\alpha = C_{j,\mathrm{out}}/C_{j,\mathrm{out}}^{\max}$ and $\beta = C_{P_j,j}/C_{j,\mathrm{out}}^{\max}$. Then,

$$\Delta F_j^w = \bar{\bar{F}}_j^w - \bar{F}_j^w = \alpha \bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j} - \beta(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) - (1-\alpha)\bar{F}_j^w. \tag{72}$$

Downstream feasibility is maintained by

$$C_{R_j,\mathrm{in}} = \frac{\bar{F}_{j,R_j} C_{j,\mathrm{out}} + F_{P_j,R_j} C_{P_j,R_j} + F^* C^*}{\bar{F}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{F}_{R_j}^w} = \frac{\bar{\bar{F}}_{j,R_j} C_{j,\mathrm{out}}^{\max} + F_{P_j,R_j} C_{P_j,R_j} + F^* C^* + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) C_{P_j,j}}{\bar{\bar{F}}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{\bar{F}}_{R_j}^w + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j})} \tag{73}$$

and

$$\bar{F}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{F}_{R_j}^w = \bar{\bar{F}}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{\bar{F}}_{R_j}^w + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}). \tag{74}$$

Simplifying common terms on both sides of Eq. (74), we get

$$\bar{F}_{j,R_j} + \bar{F}_{R_j}^w = \bar{\bar{F}}_{j,R_j} + \bar{\bar{F}}_{R_j}^w + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}). \tag{75}$$

Using Eq. (74) in Eq. (73) and simplifying, we obtain

$$\bar{\bar{F}}_{j,R_j} = \alpha \bar{F}_{j,R_j} - \beta(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}). \tag{76}$$

Using Eqs. (75) and (76) we can write

$$\Delta F^w_{R_j} = \bar{\bar{F}}^w_{R_j} - \bar{F}^w_{R_j} = (1-\alpha)\bar{F}_{j,R_j} - (1-\beta)(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}). \tag{77}$$

Finally, combining Eqs. (72) and (77), we obtain

$$\Delta W = \Delta F^w_j + \Delta F^w_{R_j} = (1-\alpha)(\bar{F}_{j,R_j} - \bar{F}^w_j - \bar{F}_{P_j,j}) \leqslant 0. \tag{78}$$

When process j is a TWP then $\bar{F}_{j,\text{out}} = 0$, by Eq. (78) we have $\Delta W = 0$. This means that a degenerated solution has been found.

To finish the proof we need to show that under the new conditions there is enough wastewater to send from process j to the set of processes R_j. That is, $\bar{\bar{F}}^w_j + \bar{\bar{F}}_{P_j,j} \geqslant \bar{\bar{F}}_{j,R_j}$.

A total mass balance on process j reads

$$\bar{F}^w_j + \bar{F}_{P_j,j} = \bar{F}_{j,R_j} + \bar{F}_{j,\text{out}}. \tag{79}$$

Then, we can write that

$$\bar{F}^w_j + \bar{F}_{P_j,j} \geqslant \bar{F}_{j,R_j}. \tag{80}$$

Adding $\bar{\bar{F}}_{P_j,j}$ to both sides of Eq. (71) and rearranging, we obtain

$$\bar{\bar{F}}^w_j + \bar{\bar{F}}_{P_j,j} + \beta(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) = \alpha(\bar{F}_{P_j,j} + \bar{F}^w_j). \tag{81}$$

Multiplying both sides of Eq. (80) by α and comparing with Eq. (81), we can write

$$\bar{\bar{F}}^w_j + \bar{\bar{F}}_{P_j,j} + \beta(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) \geqslant \alpha \bar{F}_{j,R_j}. \tag{82}$$

Finally, by Eq. (76) we obtain

$$\bar{\bar{F}}^w_j + \bar{\bar{F}}_{P_j,j} \geqslant \bar{\bar{F}}_{j,R_j}. \quad \square \tag{83}$$

Corollary 1. *In Case* I, *it is also a necessary condition of optimality that the Intermediate Process j reaches its inlet maximum concentration.*

Proof. Assume the starting solution is such that the outlet concentration of process j is already at its maximum. Then, following exactly the same proof as depicted by Eqs. (45)–(61) but replacing $C_{j,\text{out}}$ by $C^{\max}_{j,\text{out}}$, $C^{\max}_{j,\text{in}}$ can be reached without altering $C^{\max}_{j,\text{out}}$. The latter added to the fact that F_{j,R_j} can be kept constant (as shown in part b) guarantees downstream feasibility. □

Case II. Outlet concentration binding condition is

$$\left(\frac{C_{j,\text{out}}}{C^{\max}_{j,\text{in}}} - 1\right) < \frac{L_j}{\hat{F}_{P_j} C_{P_j,j}}. \tag{84}$$

In this case, an increase in $F_{P_j,j}$ to increase $C_{j,\text{in}}$ to its maximum is not possible without violating feasibility.

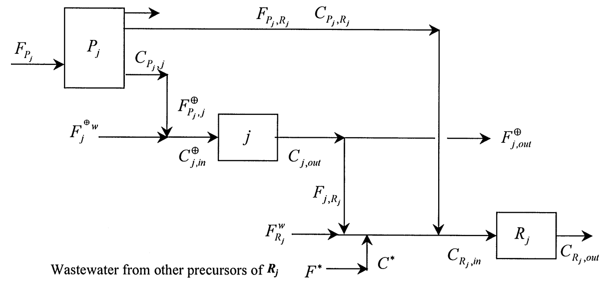

Fig. 7. Outlet concentration biding condition for Intermediate Processes.

Assume that $F_{P_j,j}$ is increased to its possible maximum value of $F^{\oplus}_{P_j,j}$ corresponding to $F_{P_j,\text{out}} = 0$. The new situation is shown in Fig. 7. The new inlet concentration in process j is $C^{\oplus}_{j,\text{in}} > C_{j,\text{in}}$.

We will now prove that it is possible to further reduce water consumption by reducing $F^{\oplus w}_j$. As a result either maximum inlet or outlet concentration will be reached first and no further water reduction will be possible. This increase needs to be accompanied by conditions to maintain feasibility downstream at the inlet of the receivers from process j. As it was done in Case I, feasibility can be obtained by keeping both $C_{R_j,\text{in}}$ and F_{R_j} constant while proving that there will be sufficient wastewater for reuse, that is $\bar{F}^{\oplus w}_j + \hat{F}_{P_j} \geqslant \bar{F}_{j,R_j}$.

We will have then two different possibilities:

(a) A reduction of the fresh water flowrate, $F^{\oplus w}_j$ will make the outlet concentration reach its maximum before the inlet does. $\bar{C}_{j,\text{out}} = C^{\max}_{j,\text{out}}$ and $\bar{C}_{j,\text{in}} < C^{\max}_{j,\text{in}}$.
(b) The inlet maximum is reached first.

The change in total water intake for both cases is

$$\Delta W = (\bar{F}^w_{R_j} - F^w_{R_j}) + (\bar{F}^{\oplus w}_j - F^{\oplus w}_j) \tag{85}$$

(a) $\bar{C}_{j,\text{out}} = C^{\max}_{j,\text{out}}$ and $\bar{C}_{j,\text{in}} < C^{\max}_{j,\text{in}}$. Performing mass balances on the component before and after the fresh water flow reduction, we obtain:

$$F^{\oplus}_{P_j,j} C_{P_j,j} + L_j = (F^{\oplus}_{P_j,j} + F^{\oplus w}_j) C_{j,\text{out}}, \tag{86}$$

$$F^{\oplus}_{P_j,j} C_{P_j,j} + L_j = (F^{\oplus}_{P_j,j} + \bar{F}^{\oplus w}_j) C^{\max}_{j,\text{out}}. \tag{87}$$

Equating the r.h.s. of these balances and using the fact that $F_{P_j,\text{out}} = 0$, i.e., $F^{\oplus}_{P_j,j} = \hat{F}_{P_j}$

$$\bar{F}^{\oplus w}_j = \left(\frac{C_{j,\text{out}}}{C^{\max}_{j,\text{out}}}\right) F^{\oplus w}_j - \left(1 - \frac{C_{j,\text{out}}}{C^{\max}_{j,\text{out}}}\right) \hat{F}_{P_j} = \alpha F^{\oplus w}_j - (1-\alpha)\hat{F}_{P_j}, \quad 0 < \alpha < 1 \tag{88}$$

where $\alpha = C_{j,\text{out}}/C^{\max}_{j,\text{out}}$. From Eq. (88) we write

$$\bar{F}^{\oplus w}_j - F^{\oplus w}_j = -(1-\alpha)(F^{\oplus w}_j + \hat{F}_{P_j}). \tag{89}$$

We now calculate $(\bar{F}^w_{R_j} - F^w_{R_j})$. Recalling that $C_{R_j,\text{in}}$ and F_{R_j} remain constant, we can write

$$F^w_{R_j} + F_{j,R_j} + F_{P_j,R_j} + F^* = \bar{F}^w_{R_j} + \bar{F}_{R_j} + F_{P_j,R_j} + F^*, \tag{90}$$

$$C_{R_j,\text{in}} = \frac{F_{j,R_j} C_{j,\text{out}} + F_{P_j,R_j} C_{P_j,R_j} + F^* C^*}{F^w_{R_j} + F_{j,R_j} + F_{P_j,R_j} + F^*} = \frac{\bar{F}_{j,R_j} C^{\max}_{j,\text{out}} + F_{P_j,R_j} C_{P_j,R_j} + F^* C^*}{\bar{F}^w_{R_j} + \bar{F}_{j,R_j} + F_{P_j,R_j} + F^*}. \tag{91}$$

Rearranging Eq. (91) and using Eq. (90) we obtain

$$\bar{F}_{j,R_j} = \frac{C_{j,\text{out}}}{C^{\max}_{j,\text{out}}} F_{j,R_j} = \alpha F_{j,R_j}. \tag{92}$$

Substituting in Eq. (90) and rearranging we get

$$\bar{F}^w_{R_j} - F^w_{R_j} = F_{j,R_j}(1-\alpha) \tag{93}$$

and therefore

$$\Delta W = (\bar{F}^w_{R_j} - F^w_{R_j}) + (\bar{F}^{\oplus_w}_j - F^{\oplus_w}_j) = (1-\alpha)(F_{j,R_j} - F^{\oplus_w}_j - F^{\oplus}_{P_j,j}) \leqslant 0. \tag{94}$$

When process j is a TWP then $F^{\oplus}_{j,\text{out}} = 0$, by Eq. (94) we have $\Delta W = 0$. This means that a degenerated solution has been found.

To finish the proof we need to show that under the new conditions there is enough wastewater to send from process j to the set of processes R_j. That is: $\bar{F}^{\oplus_w}_j + \hat{F}_{P_j} \geqslant \bar{F}_{j,R_j}$. Add $\hat{F}_{P_j}$ to both sides of Eq. (88) to obtain

$$\bar{F}^{\oplus_w}_j + \hat{F}_{P_j} = \alpha(F^{\oplus_w}_j + \hat{F}_{P_j}). \tag{95}$$

But

$$F^{\oplus_w}_j + \hat{F}_{P_j} = F_{j,R_j} + F^{\oplus}_{j,\text{out}}. \tag{96}$$

Thus, since

$$F^{\oplus}_{j,\text{out}} \geqslant 0. \tag{97}$$

We have

$$F^{\oplus_w}_j + \hat{F}_{P_j} \geqslant F_{j,R_j}. \tag{98}$$

And therefore

$$\bar{F}^{\oplus_w}_j + \hat{F}_{P_j} = \alpha(F^{\oplus_w}_j + \hat{F}_{P_j}) \geqslant \alpha F_{j,R_j}. \tag{99}$$

In addition, by Eq. (92) we obtain

$$\bar{F}^{\oplus_w}_j + \hat{F}_{P_j} \geqslant \bar{F}_{j,R_j}. \quad \square \tag{100}$$

(b) $C_{j,\text{out}} < C^{\max}_{j,\text{out}}$ and $C_{j,\text{in}} = C^{\max}_{j,\text{in}}$. Since reducing only the fresh water intake of process j cannot render the maximum outlet concentration without violating feasibility, we need to proceed exactly the same way we did in Case I and reduce both, $F^{\oplus_w}_j$ and $F^{\oplus}_{P_j,j}$. The proof is not different from the one in Case I. The same group of Eqs. (67)–(78), is used to prove the theorem and then Eqs. (79)–(83) are used to complete the feasibility proof. Thus $\Delta W \leqslant 0$. $\square$

Theorem 4 (Necessary condition of maximum concentration for terminal processes). *If the solution of the WAP problem is optimal then the outlet concentration of a Terminal Fresh Water User Process reaches its possible maximum or an equivalent solution with the same overall freshwater consumption exists.*

Proof. We will prove by contradiction that if the outlet concentration is not maximum, the maximum outlet concentration can be always reached by reducing the freshwater intake, while maintaining the inlet concentration $C_{t,\text{in}}$ constant.

Thus, assume $C_{t,\text{out}} < C^{\max}_{t,\text{out}}$. A new set of flowrates $\bar{F}_t$ and $\bar{F}^w_t$ satisfies:

$$C_{t,\text{in}} = \frac{F_{P_t,t} C_{P_t,t}}{F^w_t + F_{P_t,t}} = \frac{\bar{F}_{P_t,t} C_{P_t,t}}{\bar{F}^w_t + \bar{F}_{P_t,t}}. \tag{101}$$

Simplifying we obtain

$$\frac{F_{P_t,t}}{F^w_t + F_{P_t,t}} = \frac{\bar{F}_{P_t,t}}{\bar{F}^w_t + \bar{F}_{P_t,t}}. \tag{102}$$

Rearranging,

$$\frac{\bar{F}_t}{F_t} = \frac{\bar{F}_{P_t,t}}{F_{P_t,t}}. \tag{103}$$

However from Eq. (102)

$$F_{P_j,t}(\bar{F}^w_t + \bar{F}_{P_j,t}) = \bar{F}_{P_j,t}(F^w_t + F_{P_j,t}). \tag{104}$$

Multiplying term by term and reducing, we get

$$F_{P_j,t} \bar{F}^w_t = \bar{F}_{P_j,t} F^w_t \tag{105}$$

or

$$\frac{\bar{F}_{P_t,t}}{F_{P_t,t}} = \frac{\bar{F}^w_t}{F^w_t}. \tag{106}$$

However, by assumption,

$$\frac{F_{P_t,t} C_{P_t,t} + L_t}{F_t} = C_{T,\text{out}} < C^{\max}_{T,\text{out}} = \frac{\bar{F}_{P_t,t} C_{P_t,t} + L_t}{\bar{F}_t} \tag{107}$$

which can be rearranged to give

$$\frac{\bar{F}_t}{F_t}(F_{P_t,t} C_{P_t,t} + L_t) < \bar{F}_{P_t,t} C_{P_t,t} + L_t. \tag{108}$$

Now using Eq. (103) we get,

$$\frac{\bar{F}_{P_t,t}}{F_{P_t,t}}(F_{P_t,t} C_{P_t,t} + L_t) < \bar{F}_{P_t,t} C_{P_t,t} + L_t \tag{109}$$

or simplifying

$$\frac{\bar{F}_{P_t,t}}{F_{P_t,t}} L_t < L_t \tag{110}$$

which gives

$$\bar{F}_{P_t,t} < F_{P_t,t} \Rightarrow \frac{\bar{F}_{P_t,t}}{F_{P_t,t}} < 1. \quad (111)$$

Therefore, using Eq. (106) we get

$$\frac{\bar{F}_t^w}{F_t^w} < 1. \quad \square \quad (112)$$

5. Examples

We now show some examples from the literature and some additional ones solved using the water pinch when all these conditions are met. We also illustrate the degeneracies covered by the corollaries of the theorems.

Example 1. This example is taken from Wang and Smith (1994). The system involves four processes and their corresponding data is given in Table 1.

The minimum flowrate reported is 90.0 ton/h and two realizing network are presented in Wang and Smith (1994). Each network was obtained using a different method. The first method maximizes the concentration driving forces and the second one minimizes the number of water sources. It can be observed that, even after breaking the loops, the final designs may be of no practical use. The first method for instance, proposed a splitting of process three. If process three were an indivisible unit, such as a desalter or a reflux drum, the network would have no real meaning. However, the second method provides, after several simplifications, a realistic realizing network. It is also worth noting that before the aforementioned simplifications the flowsheet obtained was rather complex and also introduced several process splittings. Fig. 8 shows the final network obtained using method two (Wang and Smith, 1994).

According to our definitions, Process 1–3 are FWU processes while Process 4 is a WWU process. Processes 1 and 2 are head processes and Process 3 is a terminal process. There are no intermediate processes in this network. Table 2 summarizes all flowrates and final inlet and outlet concentrations of each process.

We now check if the proposed flowsheet satisfies all applicable necessary conditions of optimality.

Table 1
Example from Wang and Smith (1994)

Process number	Mass load of contaminant (kg/h)	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

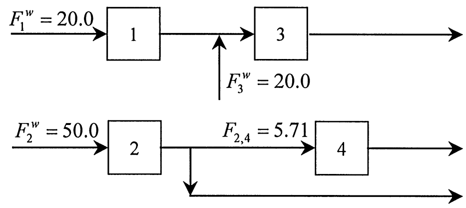

Fig. 8. Water network reported by Wang and Smith (1994).

Table 2
Final solution to Example 1

Process number	Type of process	Fresh water intake (ton/h)	Wastewater reuse (ton/h)	C_{in} (ppm)	C_{out} (ppm)
1	H	20.0	0.0	0.0	100.0
2	H	50.0	0.0	0.0	100.0
3	T	20.0	20.0	50.0	800.0
4	WWU	0.0	5.71	100.0	800.0

(Theorem 5) Monotonicity is satisfied.

Process 3 and 4 receive reusable wastewater.

1. Process 1 delivers wastewater at 100 ppm which it is fed to process 3. Process 3 has an outlet concentration of 800 ppm, therefore monotonicity is satisfied.
2. Process 2 delivers wastewater at 100 ppm to process 4. Process 4 has an outlet concentration of 800 ppm, thus monotonicity is satisfied.

(Theorem 6) Head Processes have Maximum Concentration.

Process 1 and 2 are Head Processes. Both Process 1 and 2 have outlet concentrations equal to their possible maximum. Therefore, this condition is satisfied.

(Theorem 7) Terminal Processes have Maximum Concentration.

Process 3 is a Terminal Process and its outlet concentration is at its possible maximum hence the theorem is fulfilled as well.

Consider now a different realizing network as shown in Fig. 9 (Olesen and Polley, 1997).

The total fresh water intake, 90.0 ton/h, remains unchanged. This alternative network realizes the minimum flowrate target but constitutes a degenerate solution to this example problem. This case is heeded by the Corollary of Degeneracy for Head Process. $F_{1,out} = 0$, therefore $\Delta W = 0$ and the 90.0 ton/h is an optimal solution.

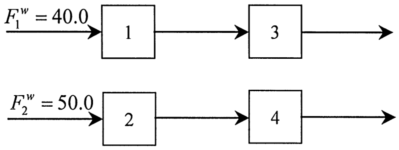

Fig. 9. Solution proposed by Olesen and Polley (1997).

Table 3
Example from Olesen and Polley (1997)

Process number	Mass load of contaminant (kg/h)	C_{in}^{max} (ppm)	C_{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

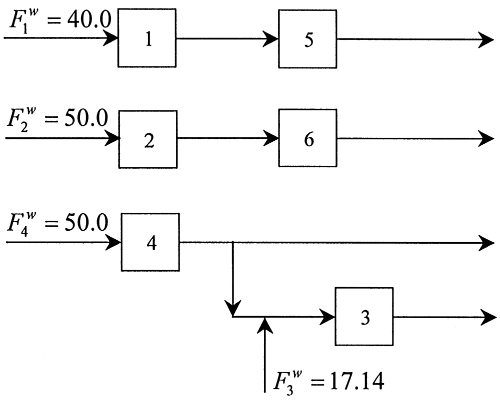

Fig. 10. Network solution for Example 2 as reported by Olesen and Polley (1997).

Observation. Process 4 is receiving all the wastewater generated in Process 2 when in reality it only needs 5.71 ton/h to complete its load removal. It does not contradict Theorem 7, as it is not a fresh water user.

Example 2. This example is taken from Olesen and Polley (1997). The system involves six processes and their corresponding data is given in Table 3.

The minimum flowrate reported is 157.14 ton/h. Olesen and Polley (1997) obtained a realizing network by methods of inspection. Fig. 10 shows this network.

Table 4 summarizes the results of this example problem for the network obtained by Olesen and Polley (1997). The target is met, so the solution is optimal but

Table 4
Degenerate solution of Example 2

Process number	Type of process	Fresh water intake (ton/h)	Wastewater reuse (ton/h)	C_{in} (ppm)	C_{out} (ppm)
1	H	40.0	0.0	0	50
2	H	50.0	0.0	0	100
3	T	17.14	5.714	25	200
4	H	50.0	0.0	0	100
5	WWU	0.0	40.0	50	800
6	WWU	0.0	5.714	100	180
Total flowrate (ton/h)		157.14	51.428		

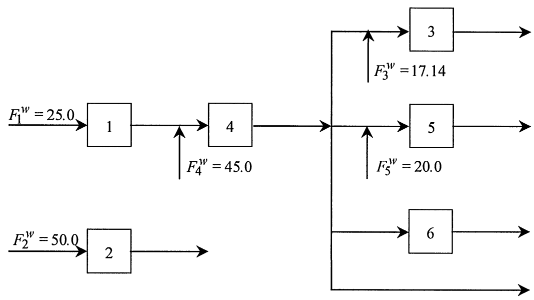

Fig. 11. Alternative solution network for Example 2.

constitutes a degeneracy of the solution network depicted in Fig. 11. The flowsheet shown in Fig. 11 satisfies all necessary conditions of optimality and meets the 157.14 ton/h target.

We now analyze each process. Process 1 is a Head Process in this network and its outlet concentration is not at its possible maximum but its wastewater is completely reused at Process 5, therefore the *degeneracy condition for head processes* is satisfied. Process 2 and 4 are also *head processes* and Theorem 2 holds in both cases.

Process 3 is the only *terminal process* in this network and satisfies Theorem 7. Besides monotonicity is also met because Process 3 receives wastewater at 100 ppm while its maximum outlet is 200 ppm.

In conclusion, the only degeneracy found in this solution is that of Process 1. In addition, when Process 1 meets the conditions of Theorem 6, Process 5 becomes a Terminal Process that satisfies the necessary condition of optimality.

Table 5 shows the results for the network depicted in Fig. 11. In this flowsheet all processes have reached both maximum inlet and outlet concentration through maximum reuse. All the necessary conditions of optimality are satisfied by this alternative solution.

Table 5
Results for the network of Fig. 11

Process number	Type of process	Fresh water intake (ton/h)	Wastewater reuse (ton/h)	C_{in} (ppm)	C_{out} (ppm)
1	H	25.0	0.0	0	80
2	H	50.0	0.0	0	100
3	T	17.14	5.714	25	200
4	I	45.0	25.0	28.57	100
5	T	20.0	20.0	50	800
6	WWU	0.0	5.714	100	800
Total flowrate (ton/h)		157.14	51.428		

6. Conclusions

Necessary conditions of optimality in water allocation problems have been presented. These conditions state that optimal structures satisfy monotonicity of the outlet concentrations when one process sends its wastewater to another. In addition, conditions under which the inlet or the outlet concentrations reach their maximum have been discussed. Future work will build on these conditions to develop a procedure to design these systems without the drawbacks of existing alternatives.

Notation

C	concentration of contaminant, ppm
$\hat{C}$	resulting concentration of contaminant if all precursor wastewater is used, ppm
$\bar{C}$	resulting concentration of contaminant after decreasing fresh water consumption, ppm
f	component flowrate, g/h
F	water flowrate, ton/h
$\hat{F}$	total wastewater flowrate from precursors, ton/h
$\bar{F}$	water flowrate after fresh water consumption reductions, ton/h

Subscripts

in	at inlet
out	at outlet
j	process j
P_j	precursors of j
R_j	receivers of j

Superscripts

min	minimum
max	maximum
$\oplus$	maximum reuse
$*$	additional sources
w	fresh water

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