On the Appropriate Modeling of Process Plant Water Systems

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DOI 10.1002/aic.11983
Published online in Wiley InterScience (www.interscience.wiley.com).

The definition of the water/wastewater allocation problem is discussed as it was originally defined by Takama et al.1 how this concept was modified, and sometimes simplified, through time, as well as additional issues that is believed are still not properly addressed. A few attempts are reviewed where parts are pointed out, and the addition of water pretreatment units are discussed, and further investigation in to the impact that proper modeling has on predictions of freshwater consumption, total annual cost and zero discharge cycles. © 2009 American Institute of Chemical Engineers

AIChe J, 56: 000–000, 2010
Keywords: water management, water/wastewater allocation

Introduction

The water allocation problem (WAP) has been extensively studied and several approaches to solve it have been presented. A comprehensive review of methods presented up to 2000 is given by Bagajewicz;2 additional overviews can be found in a few books.3,4

In general, the methods to solve the WAP can be divided into two big classes: those based on mathematical programming, and those based on graphical, heuristic or algorithmic methods. In our opinion, the most promising class is the one based on mathematical programming, originally proposed by Takama et al.1 The use of mathematical programming is being increasingly used, especially because of the inability of graphical, heuristic or algorithmic procedures to effectively provide rigorous solutions to multiple contaminant problems. Additionally, more elaborate objective functions (cost, number of connections, etc.) are easier to handle using mathematical programming approaches. We believe that sometimes, it is not that it is easier, it is the only way.

When Takama et al.1 discussed the architecture of this problem, they made sure to include a wastewater treatment subsystem and discharge concentration limits. Moreover, their model considers that the wastewater treatments could recycle water to the water-using units. Later, Wang and Smith,5 the work that gave rise to the “water pinch” method, ignored the discharge limits requirements and the aforementioned recycle. As a result, an implicit end-of-pipe treatment (EoPT) has to be assumed to comply with these requirements. Several subsequent articles,6-12 including the review made by Bagajewicz,2 have also omitted using discharge concentration limits, implicitly assuming that the end-of-pipe treatment is able to bring the concentration of the contaminants down to the discharge limits. In addition, even articles that have used the regeneration processes as means of reducing freshwater consumption, did not explicitly assume that an EoPT was present and its treated stream could be reused/recycled. For this latter case where regeneration processes are included, one cannot guarantee that an EoPT is not necessary. This is the first issue we investigate in this article.

Aside from these methodologies that model the units as mass exchangers, Gabriel and El-Halwagi12 used a source-sink model13 in which “interceptors” were included to act as regeneration processes. They assumed that each interceptor could receive water from only one source, that is, that there is no mixing before interception. This assumption allowed to discretize the efficiency of each interceptor as a function of the source only, something that rendered a linear model. In reality, the efficiency of each interceptor should be discretized as also a function of possible range of

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AIChe Journal February 2010 Vol. 56, No. 2
concentration when sources are mixed, but this was not included in their model.

Much in the same way as it was suggested by Takama et al., we argue that if an end-of-pipe treatment has to be part of the water system, its effluent should also be available as an option for reuse/recycle. In fact, there is no water system without any kind of regeneration process (even those that were classified as “end-of-pipe”). Thus, all water allocation problems must at least include one treatment unit in which its treated stream can be reused/recycled. When discussing regeneration, other articles touch on this issue, but do not explicitly come with a conclusion as strong as ours. Because of the lack of a discussion of the effect of implicitly assuming the EoPT, and, consequently, ignoring a recycle from it, there is no established knowledge, rule, as of when this practice is appropriate, and when it is not. In this article, we discuss the intricacies and consequences of ignoring the existence of at least one end-of-pipe treatment (and, consequently, the reuse/recycle of the stream treated by it), and the different architectures the WAP models should be based on.

We now turn to a second issue we want to point out regarding appropriate modeling. Most of the articles, including Takama et al., have assumed that one source of freshwater was available, usually with zero contaminant concentration, and have not included the pretreatments used to bring the freshwater to such quality. Occasionally, multiple sources of different contaminant concentration are mentioned, but rarely their use is discussed in detail, much less modeled.

Freshwater is usually sequentially processed in different pretreatment units, some producing freshwater of stringent purities (like boiler water), and some producing water with less stringent qualities. We argue that the pretreatment should be included when modeling the WAP. This system does not have to be necessarily a sequential set of treatment units where water of different quality is drawn from intermediate units, but it could be a distributed and/or decentralized system. Both the wastewater system and the pretreatment have to be modeled assuming a distributed configuration. Because the addition of these pretreatment units has not been explicitly included in the WAP previously, we discuss in this article the impact of considering them.

Finally, in addition of allowing water from the wastewater treatments (regeneration and/or EoPT) to be recycled to the water-using units, one could additionally include interaction with the pretreatment units. Ultimately, we argue that only when complete decentralization of the system is allowed, one is sure that the global optimum of the system is achieved, although such global optimum may feature centralized solutions. We also argue that when seeking zero liquid discharge cycles, this is the appropriate route to adopt.

The remaining of this article is organized as follows: we first present the problem statement and discuss different superstructures that address the recycles we discussed before, as well as the inclusion of the pretreatment units. We then present the corresponding mathematical model and analyze how each structure can be obtained from a general model. Finally, several examples are presented to illustrate the impact on freshwater usage and/or economics.

Water System Architectures and WAP Formulations

A complete water system (CWS) in process plants are typically composed of three subsystems (water pretreatment, water-using and wastewater treatment). A conventional, sequentially ordered, nonintegrated CWS is shown in Figure 1. We notice that freshwater is treated in different units in a sequential manner, lowering the concentration of key contaminants after each treatment. All units receive freshwater of a quality that corresponds to its maximum inlet concentration, and, therefore, the corresponding water is taken after each treatment. For example, WU3 may be a steam consumer, and WPT3 could be a boiler preceded by a boiler-feed treatment unit. In turn, WU4 could be a scrubbing unit that does not require boiler quality water, and WU1, WU2 could be units that have less stringent quality requirements, like for example, desalters. In some cases, freshwater, purchased or taken from natural sources can be directly used. This is illustrated by unit WU5.

Another feature of the current architecture is that all wastewaters are mixed and sent to EoPT, which is usually

Figure 1. Typical complete water system in process plants.
The boundaries of the problem (i.e., which subsystems are considered and where are their boundaries).

- The architecture of the subsystems (i.e., how their units are arranged: in series, parallel, distributed, etc.),

- Whether the recycle and reuse within subsystems is or is not allowed.

- Whether the recycle between subsystems is or is not allowed.

- The level of detail of the water-using units and/or regeneration processes models (fixed loads vs. variable loads, fixed vs. variable flowrates through the units, etc.); and

- The nature of the objective function.

The simplest form of the problem is simply a freshwater source feeding the water-using subsystem followed by an assumed end-of-pipe treatment to adjust the wastewater to below the discharge limits. This simplified version of water system is presented in Figure 2. The problem solved using this definition of the WAP is the one limited by the dashed line. Inside this line all the possible reuses among the water-using units are allowed. Here, the wastewater subsystem is treated as a single EoPT, which is not part of the optimization problem, but has to exist to bring the contaminants concentration down to the discharge limits. This is the first problem addressed by the popular technology called “water pinch”, which is very useful when a single component is assumed, and several other methods, some also used for the multicontaminant case. The objective is usually not cost, but freshwater consumption.

Wang and Smith also discussed the possibility of having regeneration processes, but they did not include a discharge limit. Thus, they implicitly assumed that an end-of-pipe treatment would help reaching these limits. We illustrate this system in Figure 3. In this case the interaction of the water-using units and some regeneration processes are allowed through three different options: reuse, regeneration-reuse and regeneration recycle. As in Wang and Smith, several subsequent articles have also used this implicit end-of-pipe treatment assumption.

Thus, in its simplest form, the problem does not explicitly consider re-using the water that is ready for discharge. We would like to point out, however, that the seminal article of the water management problem had already included such a recycle when they introduced the existence of a wastewater treatment subsystem and added discharge limits to the whole system. They state that the system showed in Figure 4 is a typical system used in refineries and is formed by two subsystems, water-using subsystem and wastewater treatment subsystem, which are often individually optimized regardless of the interaction introduced by the recycle. In reality, their definition of the wastewater subsystem together with the addition of discharge limits integrates all the possibilities of regeneration without clearly defining or singling out specifically an end-of-pipe treatment. In other words, this definition considers that the regeneration processes and the end-of-pipe treatment are part of a unique subsystem called wastewater treatment. Additionally, note that their system does not consider the existence of a water pretreatment subsystem.

Thus, when considering only these two subsystems, suggest their integration in a total system (or integrated system). Their model handled the water-using units and wastewater treatment processes assuming a decentralized model, one that has no subsystem boundaries. Although their model allows connections from any process (water-using or treatment units) to any other process, the solution they presented did not show any recycle from a regeneration unit to a water using process. The solution to their example has a water reuse subsystem followed by a wastewater treatment subsystem that is distributed.

Later, Kuo and Smith reminded of the importance of the interaction between water-using units, regeneration processes and effluent treatment system. They presented an improvement of Wang and Smith’s method, which had only considered the interaction between water-using units and regeneration processes. On the other hand, some authors have used the structure proposed by Takama et al. to solve the multiple component WAP, that is, they solved the problem that is often called total water system.

The use of the stream treated by the end-of-pipe treatment (or the addition of discharge limits) starts to play an important role not only from the freshwater consumption point of view, but also from the cost of the whole system point of view. Increasing freshwater costs, declining of water quality in the available freshwater sources and costs ratio between end-of-pipe treatment and intermediate regeneration processes can influence the trade-offs of recycling the stream treated by the end-of-pipe treatment. End-of-pipe treatment recycling can also show enormous advantages when retrofit projects are analyzed. For this case an end-of-pipe treatment already exists, and, therefore, eventuall no or very small capital cost is required.
As we stated previously, Takama et al. consider the total water system, which the water-using units and wastewater treatment processes individually interact. However, the way the subsystems interact is also important and different subsystems structures may be preferred for technical and/or layout issues. We now discuss some of these possibilities using the water system structure presented by Takama et al.: Water-using subsystem and wastewater subsystem (Figure 4).

First, we consider a water-using subsystem and a centralized/sequential wastewater treatment subsystem with a recycle of water that complies with discharge limits (Figure 5). In fact, this is the problem that should be solved when only water-using units are optimized. Note that the wastewater treatment subsystem is here understood as a single system (that could be what was previously called end-of-pipe treatment), but we allow the recycle of the discharge stream.

In Figure 6 we show a centralized/distributed wastewater treatment subsystem. In both centralized cases the centralization is more than geographical, it includes collecting all wastewaters and mixing them in one single stream before treatment.

As an alternative, one can envision a centralized and distributed wastewater treatment subsystem in the sense that no mixing of all wastewaters takes place and multiple streams feed it. This is shown in Figure 7.

Finally, Figure 8 shows a completely decentralized wastewater treatment subsystem, which is often called as integrated system (or total water system). We note that allowing flows from any treatment unit in Figure 7 to be recycled is equivalent to the system of Figure 8. In the limit, Figure 8 can be a zero-liquid discharge cycle. These are extensions of the classification proposed by Bagajewicz.

However, to achieve zero-liquid discharge cycle in the type of system presented in Figure 8, which is the most general case presented so far in the literature (including the model presented by Takama et al.), one needs to achieve certain conditions:

- Every contaminant in at least one water-using unit must have the maximum inlet concentrations higher than the lowest concentrations among the regeneration processes, and;
- Regeneration processes should be able to bring the concentration of the contaminants down to at least the lowest maximum inlet concentration of each contaminant among the water-using units.

These are conditions that are not often seen in the WAP. Current models often assume only the highest quality of freshwater available. Even when other qualities are assumed, the pretreatment processes producing the available freshwater are not considered. This is a very important opportunity when zero-liquid discharge is targeted. Note that pretreatment processes exist in the water pretreatment subsystem shown in Figure 1, and they are responsible for producing freshwater at different qualities. When considering this complete water system, the water pretreatment subsystem can receive water/wastewater from the water-using subsystem and/or from the wastewater treatment subsystem. Indeed, Figure 9a shows the architecture as it is understood nowadays, and Figure 9b shows the proposed architecture. This new architecture allows the used water to pass through the pretreatment again and so comply with the quality required by some (or all) of the water-using units. This is how the zero-liquid discharge cycle can be more easily identified.

Figure 10 shows the different definitions of the water allocation problem in relation to the boundary assumed for the analysis of the whole system, the architecture of each subsystem and the interaction among the subsystems. In other words, each of the subsystems can exhibit different options of reuse/recycle among their own units (or processes), i.e., they can be distributed systems within their own boundaries.

Figure 10a represents the optimization of the water-using subsystem only. This corresponds to the architecture presented in Figure 2. Thus, one could state this problem as follows:

*Given a set of water-using units, a set of freshwater sources with corresponding contaminant concentrations (some
Figure 9. (a) Water pretreatment subsystem sequential scheme, and (b) recycles to the water pretreatment subsystem.

usually zero), one wants to obtain a water-using network that optimizes a given objective (freshwater consumption, cost, etc.).

Figure 10b represents the optimization of the water using and treatment subsystems simultaneously. This is similar to the architectures presented in Figures 3 and 4. In the first case (Figure 3), discharge limits are not imposed and the problem could be stated as follows:

Given a set of water-using units, a set of freshwater sources with corresponding contaminant concentrations (some usually zero) and potential intermediate regeneration processes, one wants to obtain a water-using/wastewater treatment system network that optimizes a given objective (freshwater consumption, cost, etc.).

For the case presented in Figure 4, we would have the following definition:

Given a set of water-using units, a set of freshwater sources with corresponding contaminant concentrations (some usually zero), potential intermediate regeneration processes and/or a wastewater end-of-pipe treatment unit, one wants to obtain a water-using/wastewater treatment system network that complies with the discharge limits and optimizes a given objective (freshwater consumption, cost, etc.).

Note that in this later case, discharge limits is imposed, and the regeneration processes are not used only for reuse/recycle purpose, but also to condition the wastewater stream to be discharged. In the literature, the dotted box around the water using and water treatment subsystem presented in Figure 10 b is known as total water system. As stated before, this was solved by Gunaratnam et al., Karuppiah and Grossmann, Alva-Argaéz et al., Putra and Amminudin using different methodologies and assumptions.

Although all these definitions of the problem state that a set of freshwater sources is available, the issue of having more than one freshwater quality sources with different processes associated with them has not been studied yet. In fact, we can define these different freshwater qualities as part of another subsystem; the water pretreatment subsystem. The addition of this subsystem has not been investigated and can generate further trade-offs in the water allocation problem.

Figure 10c exemplifies the suggested new water allocation problem structure that we believe should be solved to completely include all the possibilities of water integration. Thus, this problem can be stated as follows:

Given a set of water pretreatment processes with their corresponding specifications, a set of water-using units, potential intermediate regeneration processes and/or a set of wastewater treatment units, one wants to obtain a water system network that complies with the discharge limits and optimizes a given objective (freshwater consumption, cost, etc.).

As in the wastewater treatment subsystem, both capital and operating cost are associated with the existence and capacity of water pretreatments that determine the availability of each quality of freshwater. One of the reasons for omitting this subsystem is the fact that such analysis only becomes relevant when cost is considered as one of the objectives. Otherwise, when freshwater consumption is the target, the source with highest quality (that is, lowest contaminant concentration) is the preferred one and this issue becomes irrelevant. It is also important to note here that the different freshwater sources are not only competing with each other, but they are competing with water reuse and/or recycles from regeneration processes.

We then conclude that the complete water integration system is obtained breaking the boundaries of the subsystems and making use of all available regeneration processes, including the ones available in the water pretreatment subsystem. In reality, when these boundaries are removed, the wastewater treatments and water pretreatments become a unique set of regeneration processes, which are now also

Figure 10. Evolution of water allocation problem regarding the boundary of the water system.

(a) Optimization of the water-using subsystem, (b) optimization of the water-using/wastewater treatment subsystems, and (c) optimization of the complete water system.)
allowed to receive freshwater. This follows the same idea of the total water system (or integrated system) previously discussed, but now we include the water pretreatment subsystem to generate a complete integrated water system.

In this article, we want to clearly establish the advantages and drawbacks of using these different formulations of the WAP and the different choices of subsystem architectures. We present the mathematical model next and discuss how to choose the aforementioned architectures, explicitly or implicitly. Later we show the potential and drawbacks of the different architectures through some examples.

The nonlinear model

The nonlinear model to solve the water allocation problem is shown in this section. In this article we consider only mass transfer water-using units (mass exchangers). However, the inclusion of non-mass transfer water-using units can be easily done. These kinds of units are often part of the class of WAP referred as source and sink models. As the name suggests, these units have the same structure of freshwater sources and sinks that have, with the addition of a link (water balance) between the source and sink corresponding to the same water-using unit, and flow rate limits.

Water balance at the water-using units

\[ \sum_w F_{WU,w} + \sum_u F_{UU,u} + \sum_r F_{RU,r} = \sum_u F_{US,u} + \sum_u F_{UU,u} + \sum_r F_{UR,r} \quad \forall u \]

(1)

where \( F_{WU,w} \) is the flow rate from freshwater source \( w \) to the unit \( u \), \( F_{UU,u} \) is the flow rates between units \( u^* \) and \( u \), \( F_{RU,r} \) is the flow rate from regeneration process \( r \) to unit \( u \), \( F_{US,u} \) is the flow rate from unit \( u \) to sink \( s \), and \( F_{UR,s} \) is the flow rate from unit to regeneration process \( r \).

Water balance at the regeneration processes

\[ \sum_w F_{WR,w} + \sum_u F_{UR,u} + \sum_r F_{RR,r} = \sum_r F_{RS,r} + \sum_r F_{RR,r} \quad \forall r \]

(2)

where \( F_{WR,w} \) is the flow rate from freshwater source \( w \) to the regeneration process \( r \), \( F_{UR,u} \) is the flow rate from regeneration process \( r^* \) to regeneration process \( r \), and \( F_{RS,s} \) is the flow rate from regeneration process \( r \) to sink \( s \). In fact, we assume here that the set of regeneration processes is formed by the set of water pretreatments and the set of wastewater treatments. If one wants to differentiate between these two sets of regeneration processes, two subsets can be easily created and different constraints applied to each subset.

Contaminant balance at the water-using units

\[ \sum_w (C_{WU,c} F_{WU,w}) + \sum_u (F_{UU,u} C_{UU,c}) + \sum_r (F_{RU,r} C_{RU,r}) = \sum_u (F_{US,u} C_{US,c}) + \sum_r (F_{UR,r} C_{UR,r}) + \Delta M_{WU} \quad \forall u, c \]

(3)

where \( C_{WU,c} \) is the concentration of contaminant \( c \) in the freshwater source \( w \), \( \Delta M_{WU} \) is the mass load of contaminant \( c \) extracted in unit \( u \), \( C_{UU,c} \) is the outlet concentration of contaminant \( c \) in unit \( u \), and \( C_{RU,r} \) is the outlet concentration of the not treated contaminant \( c \) in regeneration \( r \).

Maximum inlet concentration at the water-using units

\[ \sum_w (C_{WU,c} F_{WU,w}) + \sum_u (F_{UU,u} C_{UU,c}) + \sum_r (F_{RU,r} C_{RU,r}) \leq C_{in,max} \quad \forall u, c \]

(4)

where \( C_{in,max} \) is the maximum allowed concentration of contaminant \( c \) at the inlet of unit \( u \).

Maximum outlet concentration at the water-using units

\[ C_{out,c} \leq C_{out,max} \quad \forall u, c \]

(5)

where \( C_{out,max} \) is the maximum allowed concentration of contaminant \( c \) at the outlet of unit \( u \).

Flow rate through the regeneration processes

\[ F_{r} = \sum_w F_{WR,w} + \sum_u F_{UR,u} + \sum_r F_{RR,r} \quad \forall r \]

(6)

where \( F_{r} \) is the flow rate through the regeneration process \( r \).

Contaminant balance at the regeneration processes

\[ F_{r,c} C_{r,c} = \sum_w (F_{WR,w} C_{WU,c}) + \sum_u (F_{UR,u} C_{UU,c}) + \sum_r (F_{RR,r} C_{RR,r}) \quad \forall r, c \]

(7)

where \( C_{r,c} \) is the concentration of contaminant \( c \) in regeneration process \( r \), \( C_{RU,r} \) is the outlet concentration of contaminant \( c \) in regeneration process \( r \), and \( C_{CR,c} \) is a binary parameter that indicates if contaminant \( c \) is treated by regeneration process \( r \). We assume that \( C_{CR,r,c} \) is the concentration of the treated contaminant is known and constant.

Maximum inlet concentration of the regeneration processes

\[ C_{Rin,c} \leq C_{Rin,max,c} \quad \forall r, c \]

(9)

where \( C_{Rin,max,c} \) is the maximum concentration of contaminant \( c \) allowed at the inlet of regeneration process \( r \).

Maximum allowed discharge concentration

\[ \sum_u (F_{US,u} C_{US,c}) + \sum_r (F_{RS,s} C_{RS,s}) \leq C_{discharge,max} \quad \forall u, c \]

(10)

where \( C_{discharge,max} \) is the maximum allowed concentration at sink \( s \).
Minimum flow rates

It is well known that many solutions of the water problem may include small flow rates that are impractical. To avoid these we use the following constraints

\[ FWU_{w,u} \geq FWU_{w,u}^{\text{Min}} YWU_{w,u} \quad \forall w,u \] (11)
\[ FWR_{w,r} \geq FWR_{w,r}^{\text{Min}} YWR_{w,r} \quad \forall w,r \] (12)
\[ FUU_{a,u} \geq FUU_{a,u}^{\text{Min}} YUU_{a,u} \quad \forall u,u^* \] (13)
\[ FUS_{a,s} \geq FUS_{a,s}^{\text{Min}} YUS_{a,s} \quad \forall u,s \] (14)
\[ FUR_{a,r} \geq FUR_{a,r}^{\text{Min}} YUR_{a,r} \quad \forall u,r \] (15)
\[ FRU_{r,u} \geq FRU_{r,u}^{\text{Min}} YRU_{r,u} \quad \forall r,u \] (16)
\[ FRR_{r,r} \geq FRR_{r,r}^{\text{Min}} YRR_{r,r} \quad \forall r,r^* \] (17)
\[ FRS_{r,s} \geq FRS_{r,s}^{\text{Min}} YRS_{r,s} \quad \forall r,s \] (18)

which uses a set of binary variables \((YWU_{w,u}, YWR_{w,r}, YUU_{u,u^*}, YUS_{a,s}, YUR_{a,r}, YRU_{r,u}, YRR_{r,r}, \text{ and } YRS_{r,s})\) that are equal to one when the corresponding flow rate is different from zero and zero otherwise.

Maximum flow rates

To ensure that the connections do not surpass maximum values, we use the following constraints

\[ FWU_{w,u} \leq FWU_{w,u}^{\text{Max}} YWU_{w,u} \quad \forall w,u \] (19)
\[ FWR_{w,r} \leq FWR_{w,r}^{\text{Max}} YWR_{w,r} \quad \forall w,r \] (20)
\[ FUU_{a,u} \leq FUU_{a,u}^{\text{Max}} YUU_{a,u} \quad \forall u,u^* \] (21)
\[ FUS_{a,s} \leq FUS_{a,s}^{\text{Max}} YUS_{a,s} \quad \forall u,s \] (22)
\[ FUR_{a,r} \leq FUR_{a,r}^{\text{Max}} YUR_{a,r} \quad \forall u,r \] (23)
\[ FRU_{r,u} \leq FRU_{r,u}^{\text{Max}} YRU_{r,u} \quad \forall r,u \] (24)
\[ FRR_{r,r} \leq FRR_{r,r}^{\text{Max}} YRR_{r,r} \quad \forall r,r^* \] (25)
\[ FRS_{r,s} \leq FRS_{r,s}^{\text{Max}} YRS_{r,s} \quad \forall r,s \] (26)

Objective functions

Minimum freshwater consumption

\[ \text{Min} \sum_w \left( \sum_u FWU_{w,u} + \sum_r FWR_{w,r} \right) \] (27)

Minimum total annual cost

\[ \text{Min} \left[ OP \left( \sum_w \sum_u a_w \left( \sum_u FWU_{w,u} + \sum_r FWR_{w,r} \right) \right) \right. \] (28)

\[ + \sum_r OP_r FR_r - \alpha f FC \right] \]

where \(OP_r\) are the operational cost of the regeneration processes, \(OP\) is the hours of operation per year. The last term is the annualized capital cost, where \(FC\) is the fixed capital cost and \(\alpha f\) is any factor that annualizes the capital cost (usually 1/N, where N is the number of years of depreciation). The fixed capital of investment is calculated using the sum of the piping costs and the new regeneration units costs as follows

\[ FC = \sum_u \left( \frac{\sum_w YWU_{w,u} CCWU_{w,u} + \sum_r YUR_{r,u} CCRU_{r,u}}{r} \right) \] (29)

which uses a set of capital cost parameters to assign cost to the connections \((CCWU_{w,u}, CCRU_{r,u})\) and \((CCUU_{w,u}, CCRS_{r,s})\) and the regeneration processes \((CCR_r)\).

All the aforementioned equations need to be tailored to the specifics of each system. If one considers the conventional problem stated by Takama et al.\(^1\) that is, the one in which the water pretreatment subsystem is not considered, \(FWR_{r,s}\) does not exist, and, thus, should be set to zero. In this case all the regeneration processes are part of the wastewater treatment subsystem. In the same way, when only the water-using units are considered, all the parameters that relate regeneration processes should be set as zero.

Another point that should be made here is related to the interactions among the subsystems and their boundaries. Again, we take the case in which we have the only water-using subsystem and the wastewater treatment subsystem (Figures 5 to 8).

- In the case of the system of Figure 5, that is, for a centralized treatment system with fixed structure, but now with the recycle allowed, we set \(FUS_{a,s}\) to zero and we consider only one treatment with all fixed outlet concentrations, which can be the called end-of-pipe treatment. Thus, considering the end-of-pipe treats all the involved contaminants, Eqs 7 and 8 are not necessary and \(CRF_{r,s}\) can be substituted by \(CF_{r,s}\), which is a parameter.

- In the case of the system of Figure 6, the treatment is centralized but it can be individually optimized. In fact, for this system the water using subsystem could be first optimized, and then the treatment subsystem is optimized utilizing the output of the water subsystem as input of the wastewater treatment subsystem. However, a better procedure would be to optimize both systems as separate subsystems while a connection between them still exist. To achieve that, we introduce a fictitious unit \(u_r\). This unit is actually a mixer and has \(\Delta M_{u,r} = 0\) for all contaminants. The connection between the two systems is done allowing only the fictitious unit to send water/wastewater to the wastewater treatment units: \(FUS_{a,s} = 0 \forall u,s, FUR_{a,r} = 0 \forall u \neq u_r, r\). Because this case allows only the final stream to be recycled (the one leaving the wastewater treatment subsystem), we also introduce a fictitious regeneration process \(r_f\) with all \(XCR_{r,f} = 0\) (none of the contaminants are treated, it is only a mixer),
Table 1. Limiting Data for Example 1

<table>
<thead>
<tr>
<th>Process Number</th>
<th>Mass Load of Contaminant (kg/h)</th>
<th>(C_{in}) (ppm)</th>
<th>(C_{out}) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>50</td>
<td>800</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>400</td>
<td>800</td>
</tr>
</tbody>
</table>

and we then make \(FRS_{r,s} = 0 \forall r \neq r, s\), as well as \(FRU_{r,u} = 0 \forall r \neq r, u\). This kind of system may be considered when the subsystems are far apart and layout is an issue, especially for retrofits.

- In the case of Figure 7, we keep the concepts presented for Figure 3, but the fictitious unit is no longer needed. On the other hand, the fictitious regeneration is still needed. In the case of Figure 8, we keep all our equations and no fictitious units/processes are needed.

Illustrations

We first present a single contaminant case, which was originally solved as a water-using unit subsystem problem (no regeneration processes—pretreatment and/or wastewater treatment—and, consequently, no discharge limits). With this example we show that freshwater consumption can be reduced if the recycle of the end-of-pipe treatment is allowed.

In example 2, we extend the previous example allowing the addition of a regeneration process from the wastewater treatment subsystem. In this example, we show that even if the recycle of the end-of-pipe treatment does not show any advantage from the freshwater consumption point of view, it can sometimes bring reductions in costs.

In a third example, we suggest a modification of the single contaminant case in which the water pretreatment subsystem is considered. Thus, we show the impact of considering this subsystem.

Example 4 shows a small multicontaminant water-using subsystem example in which there is a reduction in freshwater consumption when the reuse/recycle of the EoPT is considered.

Then a larger multiple contaminant problem is analyzed (examples 5 to 7). This problem was originally solved without discharge limits. We present networks that have different arrangements of the pretreatment subsystem, water-using subsystem and wastewater treatment subsystem. We show that the recycle of the stream treated by the end-of-pipe treatment can also reduce costs and the addition of the pretreatment subsystem can generate possibilities of zero discharge cycles.

The examples were solved using GAMS/DICOPT. Because some of the examples could not be solved directly in DICOPT, starting points were generated using a linear relaxation of the nonlinear model. The relaxed model was built using the convex and concave envelopes of the bilinear terms\(^{23}\) and linear underestimators for the concave terms, and was solved using GAMS/CPLEX.

Example 1

Example 1 is a single contaminant network adapted from Wang and Smith\(^5\), which they solved using pinch analysis. The limiting process data for this problem are shown in Table 1, and it has a freshwater consumption without reuse (conventional network configuration) of 112.5 t/h.

When the end-of-pipe recycling is not allowed, the freshwater consumption can reach a minimum of 90 t/h. With the recycle (assuming an end-of-pipe exit concentration of 5 ppm), the minimum consumption is 20 t/h. This minimum consumption could also be calculated using the “water-pinch” graphical method as shown by Wang and Smith\(^5\).

Although the water pinch is also able to perform the design of this single component network complying with minimum consumption, costs cannot be used to drive the design. One could consider several network possibilities (degenerate solutions, that is, different network structures that are able to achieve minimum consumption) and then compare their costs, but in this case there is no guarantee that all possibilities are analyzed. Moreover, if one wants the optimum network from the cost point of view the resulting network does not have to operate at minimum freshwater consumption. Therefore, the number of options to be analyzed is much larger, and the likelihood to miss the optimal network is smaller, not to mention the amount of work involved.

We now analyze this problem using economic objectives. Freshwater is assumed to be \(x_i($/t) = 0.3\), and the system operates 8,600 h per year. There is one freshwater source, which is free of contaminants, and the end-of-pipe treatment has an outlet concentration of 5 ppm, which is the maximum concentration allowed for disposal. The operating cost of the end of pipe treatment is \(OPN_i($/t) = 1.0067\), and the investment cost is \(CCR_i ($/t^{0.7}) = 19,400\). The capital costs with connections are presented in Table 2.

Both the grassroots design and the retrofit of this network are analyzed in this first example. For the retrofit case, it is assumed that a conventional network (no water reuse) is the starting point, that is, the current network has only the

Table 2. Capital Costs of the Connections

<table>
<thead>
<tr>
<th>Unit 1</th>
<th>Unit 2</th>
<th>Unit 3</th>
<th>Unit 4</th>
<th>End of Pipe Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>FW</td>
<td>$39,000</td>
<td>$76,000</td>
<td>$47,000</td>
<td>$92,000</td>
</tr>
<tr>
<td>Unit 1</td>
<td>–</td>
<td>$150,000</td>
<td>$110,000</td>
<td>$45,000</td>
</tr>
<tr>
<td>Unit 2</td>
<td>$50,000</td>
<td>–</td>
<td>$134,000</td>
<td>$42,000</td>
</tr>
<tr>
<td>Unit 3</td>
<td>$180,000</td>
<td>$35,000</td>
<td>–</td>
<td>$98,000</td>
</tr>
<tr>
<td>Unit 4</td>
<td>$163,000</td>
<td>$130,000</td>
<td>$90,000</td>
<td>–</td>
</tr>
<tr>
<td>EoPT</td>
<td>$83,000</td>
<td>$102,500</td>
<td>$98,000</td>
<td>$124,000</td>
</tr>
</tbody>
</table>
connection between the water source and units and between units and the end-of-pipe treatment without any reuse among units or recycle of the water treated by the end-of-pipe treatment. The costs previously presented are used in the retrofit case as well. However, the capital cost of existing connections (between freshwater and water using units and water using units and end-of-pipe treatment), and processes (in this case the end-of-pipe treatment) are set to zero. Finally, when retrofitting, one has to assume that any increase in water throughput in the EoPT is possible (there is extra capacity installed), or has to put a limit to the maximum capacity, especially when recycles that were not present in the first place are now allowed. In our case, we consider the capacity of the EoPT as being the volumes of wastewater treated by the conventional network (112.5 t/h). We first obtain the networks for minimum cost (TAC) using Eqs. 28 and 29, but featuring the minimum freshwater consumption without recycles. Notice that in this situation the operating costs are fixed, because the freshwater consumption and the EoPT flow rates have been fixed (there is no recycle). The networks obtained for the grassroots design and retrofit case are presented in Figures 11 and 12, respectively.

Allowing the option of recycling the stream treated by the end-of-pipe treatment reduces the minimum freshwater consumption to 20 t/h. This represents a reduction of approximately 78% in freshwater consumption, which is very significant. Figures 13 and 14 show the minimum TAC networks at their minimum consumption (20 t/h) for grassroots design and retrofit case, respectively.

Example 2

Example 2 is a special case of Example 1 in which the addition of a regeneration process is allowed. It has a capital cost of $CCR_c = 16,800$, and the operational cost is assumed to be $OCN (t/h) = 1.00$. This regeneration process has a fixed outlet concentration of 10 ppm.

The capital costs of connections involving the regeneration process are presented in Table 3 and the minimum TAC is calculated in the same way as in example 1.

The grassroots design case is investigated first. Now, both cases of allowing and not allowing the recycle of the end-of-pipe treatment stream can reach the minimum freshwater consumption of 20 t/h. Unlike Example 1, this example does not show any advantage of allowing end-of-pipe recycling when looked from the minimum freshwater consumption perspective. However, advantages may be seen when the total annualized cost (TAC) is minimized. The minimum TAC obtained for the case in which the end-of-pipe recycling is not allowed (Figure F15) is $1,013,429$ per year. When the end-of-pipe recycle is allowed, the minimum TAC decreases to $969,237$ per year, which is 4.4% less than the former case. This is the network presented in Figure 13, obtained when consumption was minimized.

Note that when the recycle of the stream treated by the end-of-pipe treatment is allowed, the minimum freshwater consumption can be achieved without using the available regeneration process.

Next, the retrofit design for the given network is analyzed. As before, a conventional network (no water reuse) is assumed. In this case, the current network does not have any intermediate regeneration process. The only existing connections are the ones between the freshwater source(s) and the water-using units, and between water-using units and the end-of-pipe treatment. This has the format of a conventional water system, which consumes 112.5 t/h. A similar structure is presented in Figure 1, but here the water pretreatment subsystem is only defined by a freshwater source, and the wastewater treatment subsystem is only defined by an end-of-pipe treatment.
In both cases, with and without end-of-pipe recycle, the minimum freshwater consumption can be brought down to 20 t/h. This solution is expected because the minimum freshwater consumption problem for a retrofit renders the same solution that the grassroots problem (Figure 15). The biggest challenge when retrofit is the target is to have the less costly (or more profitable) design. Faria and Bagajewicz showed that for the retrofit case one can maximize savings instead of minimizing total annualized cost. The maximum savings at the minimum consumption of the network presented in Figure 16 (no EoPT treatment allowed) is $289,399 per year. If recycle of end-of-pipe is allowed (Figure 17), the saving goes up to $366,550 per year, which is approximately 27% higher.

Example 3

In this example, we discuss the suggested complete water system using a single contaminant problem. We start with the simplest form of the complete water system which assumes that the water pretreatment subsystem cannot receive water from the other two subsystems. In this case, the pretreatment subsystem is added without allowing it to receive streams from the other two subsystems. However, the water-using subsystem and wastewater treatment subsystem are handled as in the total water system previously discussed. The limiting data is presented in Table 4. Note that unit two has a maximum outlet concentration of 20 ppm, and the end-of-pipe treatment has an outlet concentration of 25 ppm, which coincides with the discharge limit. We used the same capital and operating cost of the end-of-pipe treatment, as well as connection costs of Example 1.

One external freshwater source is used, but two water treatment units are considered thus providing two different qualities of freshwater. In other words, the pretreatment subsystem is a sequential system that does not necessarily need to treat all freshwater to the highest quality. This is the scheme presented in Figure 9a.

Note that there is also the possibility of recycling water from the water-using subsystem and/or wastewater treatment subsystem to the water pretreatment subsystem (Figure 9b). However, this is analyzed later in this example.

In this first case we assume that pretreatment 1 can bring the freshwater down to 10 ppm, and pretreatment 2 can further treat it down to 0 ppm. Pretreatment 1 has an operating cost of $0.30/t and a capital cost of $8,500/t. The maximum inlet concentration of this pretreatment is 500 ppm. The operating cost of pretreatment 2 is $0.50/t, and the capital cost is $10,500/t. Pretreatment 2 has a maximum inlet concentration of 20 ppm. With the exception of capital cost, this problem could be solved using the conventional total water system model: Eqs. 1 through 27, and TAC given by the sum of operating costs (Eq. 28), and the annualized FCI, in turn given by Eq. 29. Then, we would have to consider two sources of water with different qualities and different costs. Thus, the two pretreatment units would be eliminated from the problem description and the only regeneration processes existing in this problem would be the ones that are part of the wastewater treatment subsystem.

Figure 18 shows the solution found when the complete water system is solved assuming sequential water pretreatment and the total annual cost is minimized. Recycles from the water-using units to the water pretreatment units are not

Table 3. Capital Costs of the Connections

<table>
<thead>
<tr>
<th></th>
<th>Unit 1</th>
<th>Unit 2</th>
<th>Unit 3</th>
<th>Unit 4</th>
<th>Reg.</th>
<th>End of Pipe Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>FW</td>
<td>$39,000</td>
<td>$76,000</td>
<td>$47,000</td>
<td>$92,000</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Unit 1</td>
<td>$50,000</td>
<td>$150,000</td>
<td>$110,000</td>
<td>$45,000</td>
<td>$145,000</td>
<td>$83,000</td>
</tr>
<tr>
<td>Unit 2</td>
<td>–</td>
<td>$134,000</td>
<td>–</td>
<td>$40,000</td>
<td>$37,000</td>
<td>$102,500</td>
</tr>
<tr>
<td>Unit 3</td>
<td>$180,000</td>
<td>$35,000</td>
<td>–</td>
<td>$42,000</td>
<td>$91,000</td>
<td>$98,000</td>
</tr>
<tr>
<td>Unit 4</td>
<td>$163,000</td>
<td>$130,000</td>
<td>$90,000</td>
<td>–</td>
<td>$132,000</td>
<td>$124,000</td>
</tr>
<tr>
<td>Reg.</td>
<td>$33,000</td>
<td>$130,000</td>
<td>$50,000</td>
<td>$98,000</td>
<td>–</td>
<td>$45,000</td>
</tr>
<tr>
<td>EoPT</td>
<td>$83,000</td>
<td>$102,500</td>
<td>$98,000</td>
<td>$124,000</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 15. Grassroots network design for Example 2—no EoPT recycle—minimum TAC at minimum consumption.
Figure 16. Retrofit network design for Example 2—no EoPT recycle—Minimum TAC at minimum consumption.

Figure 17. Retrofit network design for Example 2—EoPT recycle allowed—minimum TAC at minimum consumption.

allowed here. Figure 18 shows that both types of freshwater are used, and that freshwater treated by only pretreatment 1 is mixed with the recycle of the end-of-pipe treatment before it feeds unit 2. This network has a TAC of $1,275,915.

The same problem can be solved using the common assumption of one freshwater source free of contaminants. This is accomplished by disallowing any split after WPT 1 and forcing the use of water from WPT 2.

The minimum TAC found was $1,309,950, and the network found is shown in Figure 19. It is the same as in the case of Figure 18 (except of course for the pretreatment, which has been forced to be sequential). The two networks, however, differ substantially in the freshwater consumption. If one looks at this problem from the freshwater consumption point of view, the solution presented in Figure 19 is better than the one in Figure 18. However, in Figure 19 the overall cost of the water pretreatment system is higher than the one in Figure 18. This new trade-off created by the addition of the water pretreatment subsystem is one of the reasons why the complete water system becomes very important when costs are analyzed.

We conclude here that ignoring the modeling and constraints emerging from pretreatment and seeking minimum freshwater consumption, or even minimum TAC, leads to the wrong solution.

We also investigated forbidding the recycle of the end-of-pipe treatment in the previous cases. Figure 20 shows the solution, which features a total annual cost of $1,314,652 consuming 97.78 t/h. For the integrated system scheme case (which allows the recycle of the EoPT), the optimum network found has a TAC of $1,536,684 and consumes 90 t/h of freshwater. This network has the same structure presented in example 1 (Figure 11) and, is, therefore, not presented again.

We now consider the complete integrated water system, which allows all interactions within subsystems and between subsystems. In other words, this case considers each pretreatment, water-using unit and wastewater treatment as a single process inside one only boundary that is the complete water system. The solution of this case is presented in Figure 21. This network has a zero liquid discharge cycle and a total annualized cost of $410,277. Note that allowing the integration of the water pretreatment subsystem eliminates the existence of the end-of-pipe treatment.

Example 4

We now present a simple multicontaminant example from Wang and Smith. This example has two water-using units and two contaminants, and minimum freshwater consumption is the target. The example is meant to show that the same effects as in single contaminant cases are observed.

Table 5 presents the limiting data of this problem. The minimum freshwater consumption of this network without reuse is 63.33 t/h.

Because no regeneration process exists in this example, only two cases are analyzed: first, the case in which there is no recycle of the end-of-pipe treatment; and second the case where the stream treated by the end-of-pipe treatment can be reused by the water using units.

For the end-of-pipe treatment is assumed outlet concentration of 10 ppm for both contaminants. These concentrations are in agreement with the maximum allowed for disposal.

Consider the first case where no recycle of end-of-pipe treatment is allowed. The minimum freshwater consumption is 54 t/h, which is approximately 15% less than the freshwater usage without integration (straight use of freshwater in all units). The 54 t/h freshwater consumption network is presented in Figure 22.

The minimum freshwater consumption can be further reduced when the recycle of the stream treated by the end-of-pipe treatment is allowed. Indeed, the answer is that 40 t/h of freshwater are needed. This is 26% lower than the previous case (and 36.8% lower than the consumption without reuse). The network corresponding to 40 t/h freshwater consumption is presented in Figure 23.

Table 4. Limiting Data for Example 3

<table>
<thead>
<tr>
<th>Process Number</th>
<th>Mass Load of Contaminant</th>
<th>( C_{in} ) (ppm)</th>
<th>( C_{out} ) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 kg/h</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>5 kg/h</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>30 kg/h</td>
<td>50</td>
<td>800</td>
</tr>
<tr>
<td>4</td>
<td>4 kg/h</td>
<td>400</td>
<td>800</td>
</tr>
</tbody>
</table>
recycle, and, therefore, it has a higher capital cost and may have also a higher operating cost.

The increase in capital cost due to the increase of end-of-pipe treatment capacity can be an important factor for networks. The influence of this increase can only in reality be observed when all the portions of capital cost (other regeneration processes, piping, etc) are also simultaneously considered. In this example, the influence seems to be significant (the end-of-pipe treatment now treats 9.34 t/h more than in the case of reuse without recycle). In addition, both options have the same number of connections. On the other hand, if this is a retrofit project and the end-of-pipe treatment already exists, the capital cost would only be related to new connections (assuming the original network had no reuse and therefore the available end-of-pipe treatment would be 63.33 t/h).

### Table 5. Limiting Data of Example 4

<table>
<thead>
<tr>
<th>Process</th>
<th>Contaminant</th>
<th>Mass Load (kg/h)</th>
<th>Contmax (ppm)</th>
<th>Contmin (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>4</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>25</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>5.6</td>
<td>80</td>
<td>240</td>
</tr>
<tr>
<td>B</td>
<td>2.1</td>
<td>30</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>
In this case, the option allowing end-of-pipe treatment recycling needs only one extra pipe, which may not be a significant extra capital. The importance of having a capital cost should be investigated together with the benefits obtained with each option, which economically can be related to the operating cost. Here, the operating cost favors the non-recycling option once the ratio between cost of freshwater and end-of-pipe treatment cost decreases. In fact, when economics is the driven factor, all these issues should be considered together in a more general measurement such as total annualized cost, net present value (NPV), and/or return on investment (ROI). Some of these objectives will be addressed in the next few examples.

Example 5

Example 5 is applied to a refinery case presented by Koppol et al. This example has four key contaminants (salts, H2S, Organics and ammonia) and six water-using units. The limiting data of the water-using units are shown in Table 6. This network without reuse (conventional network) consumes 144.8 t/h of freshwater. The discharge limits are: 15 ppm for salts, 5 ppm for H2S, 45 ppm for Organics and 20 ppm for ammonia. The existing end-of-pipe treatment is able to reduce the contaminant to these discharge limits, and no concentration limit is imposed at the treatment inlet.

Some of the different cases previously described are discussed in this example: First we consider the water-using subsystem only. Then, we include interactions with the wastewater subsystem. Finally, the pretreatment subsystem is considered and the complete water system is investigated. Consideration of recycling (or not) the stream treated by an end-of-pipe treatment are also made for all the aforementioned cases.

Case 1: Water-using Subsystem only. In this case only the water-using units and the conventional end-of-pipe treatment are assumed. The original problem solved by Koppol et al. had an implicit end-of-pipe treatment, that is, it did not include it in the problem and so the recycle of the stream treated by the EoPT was not considered. We investigate both cases here.

The minimum freshwater consumption achieved when end-of-pipe recycling is not allowed is 119.332 t/h. The minimum total annual cost (TAC) is found to be $2,291,652, which is also a network that consumes 119.332 t/h of freshwater. The solution is presented in Figure 24.

When end-of-pipe recycling is allowed, the minimum consumption is 33.571 t/h, which is approximately 72% lower than the earlier solution. The minimum TAC ($2,062,797) for this case is also found featuring the minimum freshwater consumption (33.571 t/h). Figure 25 shows the network corresponding to this solution.

Case 2: Interaction between Water-using and Wastewater Treatment Subsystems allowed. The previous example is now solved for the case in which the wastewater treatment

![Figure 22. Grassroots network design for Example 4—no EoPT recycle.](image-url)

![Figure 23. Grassroots network design for Example 4—EoPT recycle allowed.](image-url)

### Table 6. Water-Using Units Data of Example 5

<table>
<thead>
<tr>
<th>Process</th>
<th>Contaminant</th>
<th>Load (kg/h)</th>
<th>C_{in,max} (ppm)</th>
<th>C_{out,max} (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - Caustic</td>
<td>Salts</td>
<td>0.18</td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>Treat</td>
<td>Org</td>
<td>1.2</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>H2S</td>
<td>0.75</td>
<td>5000</td>
<td>10000</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>0.1</td>
<td>1500</td>
<td>3000</td>
</tr>
<tr>
<td>2 - Distillation</td>
<td>Salts</td>
<td>3.61</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Org</td>
<td>100</td>
<td>1</td>
<td>4000</td>
</tr>
<tr>
<td></td>
<td>H2S</td>
<td>0.25</td>
<td>0</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>0.8</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>3 - Amine</td>
<td>Salts</td>
<td>0.6</td>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Org</td>
<td>30</td>
<td>1</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>H2S</td>
<td>1.5</td>
<td>0</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>1</td>
<td>0</td>
<td>3500</td>
</tr>
<tr>
<td>4 - Merox-I</td>
<td>Salts</td>
<td>2</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>Org</td>
<td>60</td>
<td>200</td>
<td>6000</td>
</tr>
<tr>
<td></td>
<td>H2S</td>
<td>0.8</td>
<td>50</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>1</td>
<td>1000</td>
<td>3500</td>
</tr>
<tr>
<td>5 - Hydrotreating</td>
<td>Salts</td>
<td>3.8</td>
<td>85</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>Org</td>
<td>45</td>
<td>200</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>H2S</td>
<td>1.1</td>
<td>300</td>
<td>6500</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>2</td>
<td>200</td>
<td>1000</td>
</tr>
<tr>
<td>6 - Desalting</td>
<td>Salts</td>
<td>120</td>
<td>1000</td>
<td>9500</td>
</tr>
<tr>
<td></td>
<td>Org</td>
<td>480</td>
<td>1000</td>
<td>6500</td>
</tr>
<tr>
<td></td>
<td>H2S</td>
<td>1.5</td>
<td>150</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>Ammonia</td>
<td>0</td>
<td>200</td>
<td>400</td>
</tr>
</tbody>
</table>
subsystem is also included. There are other three regeneration processes available in this wastewater treatment subsystem: Reverse osmosis, which reduces salts to 20 ppm; API separator followed by ACA, which reduces organics to 50 ppm; and, Chevron wastewater treatment, which reduces \( \text{H}_2\text{S} \) to 5 ppm and ammonia to 30 ppm.

First we present solutions for a centralized sequential wastewater treatment system (as in Figure 5). For both solutions (allowing and not allowing the end-of-pipe recycling) the minimum freshwater consumption is 33.571 t/h. Freshwater cost is $0.32/t, and the plant operates 8,600 h per year. The end-of-pipe treatment has a capital cost of $30,000/t\(^{0.7}\) and an operating cost of $1.80/t. The costs of the potential additional regeneration processes are presented in Table 7.

The costs of connections are presented in Table 8. Only the costs from the units to the centralized system are considered. The costs of connections between regeneration processes are ignored.

We start analyzing the case in which the wastewater treatment subsystem is sequential and centralized. The minimum total annual cost of the networks that are able to operate at minimum freshwater consumption is obtained both when end-of-pipe recycling is allowed and when it is not. Figure 26 shows the centralized sequential regeneration system network in which end-of-pipe recycling is not allowed. This network has a total annual cost of $2,065,383. When end-of-pipe recycling is allowed (Figure 27), the total annual cost goes down to $1,292,425, which represents only 37% of the previous value. Note that, allowing the end-of-pipe recycling, only API separator is needed as additional regeneration process.

The minimum TAC is also obtained without forcing the minimum consumption. The same solution is found for the case in which the end-of-pipe recycling is allowed (Figure 27). However, for the case in which the recycle of the end-of-pipe treatment is not allowed, the minimum TAC happens at a freshwater consumption larger than the minimum (38.983 t/h). This network is presented in Figure F28. It has a total annual cost of $1,351,259, and uses two of the three available additional regeneration processes.

Now, the centralized distributed system is analyzed (as in Figure 6). The solution for minimum TAC without recycle of the end-of-pipe treatment is presented in Figure F29. Note that again the minimum TAC for this case does not happen at the minimum freshwater consumption of the system. This network also operates at 38.983 t/h, and has a TAC of $1,330,142. Like the previous case, the suggested network has two regeneration processes. The major difference is due.

### Table 7. Costs of the Wastewater Treatments for Example 5

<table>
<thead>
<tr>
<th>Wastewater Treatments</th>
<th>Capital Cost ($/t(^{0.7}))</th>
<th>Operating Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>API separator followed by ACA</td>
<td>$25,000</td>
<td>0.12</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>$20,100</td>
<td>0.56</td>
</tr>
<tr>
<td>Chevron wastewater treatment</td>
<td>$16,800</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Figure 24. Grassroots network design for Example 5—No regeneration processes included—no EoPT recycle—minimum TAC.

Figure 25. Grassroots network design for Example 5—No regeneration processes included—EoPT recycle allowed—minimum TAC.
to the distributed system that allows different flow rates to be treated by the different regeneration processes.

When end-of-pipe recycling is allowed, the minimum TAC is found to feature the minimum consumption. This network is the same found when centralized sequential system was analyzed (Figure 27).

Analyzing the network presented in Figure 29, the minimum TAC is also minimized maintaining the freshwater consumption at the minimum possible. This solution is presented in Figure 30, and has a total annual cost of $1,476,784. All the three additional regeneration processes are needed in this case.

Now the integrated system is considered (as in Figure 8). Both cases, allowing and not allowing the recycle of the stream treated by the end-of-pipe treatment, can reach a minimum freshwater consumption of 33.58 t/h.

Table 8. Capital Costs of the Connections for Example 5

<table>
<thead>
<tr>
<th>$(x10^3)$</th>
<th>U1</th>
<th>U2</th>
<th>U3</th>
<th>U4</th>
<th>U5</th>
<th>U6</th>
<th>Centralized System</th>
<th>EOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>23</td>
<td>50</td>
<td>18</td>
<td>63</td>
<td>16</td>
<td>25</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>U1</td>
<td>-</td>
<td>50</td>
<td>110</td>
<td>45</td>
<td>70</td>
<td>42</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>U2</td>
<td>-</td>
<td>-</td>
<td>34</td>
<td>40</td>
<td>11</td>
<td>35</td>
<td>5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>U3</td>
<td>110</td>
<td>34</td>
<td>-</td>
<td>42</td>
<td>60</td>
<td>18</td>
<td>6.2</td>
<td>6.2</td>
</tr>
<tr>
<td>U4</td>
<td>45</td>
<td>40</td>
<td>42</td>
<td>-</td>
<td>23</td>
<td>34</td>
<td>7.8</td>
<td>7.8</td>
</tr>
<tr>
<td>U5</td>
<td>70</td>
<td>11</td>
<td>60</td>
<td>23</td>
<td>-</td>
<td>28</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>U6</td>
<td>42</td>
<td>35</td>
<td>18</td>
<td>34</td>
<td>28</td>
<td>-</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Centralized System</td>
<td>5.3</td>
<td>5.1</td>
<td>6.2</td>
<td>7.8</td>
<td>5.8</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EOP</td>
<td>5.3</td>
<td>5.1</td>
<td>6.2</td>
<td>7.8</td>
<td>5.8</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 26. Grassroots network design for Example 5—Centralized sequential regeneration processes—no EoPT recycle—Minimum TAC at minimum consumption.

Figure 27. Grassroots network design for Example 5—centralized sequential regeneration processes—EoPT recycle allowed—minimum TAC at minimum consumption.
Networks corresponding to the case in which end-of-pipe recycling is not allowed are presented in Figures F31, F32, respectively. The first one has the minimum total annual cost ($1,093,011), which has a freshwater consumption (38.876 t/h) higher than the minimum possible. The second (Figure 32) gives the minimum TAC of $1,123,957. This solution is found for a network that operates at the minimum freshwater consumption for this system. Once again, the former
case requires only two of the three regeneration process while the later needs all of the three regeneration processes to allow the minimum freshwater consumption.

When end-of-pipe recycling is allowed in the total water system scheme, the minimum total annualized cost becomes $1,065,451. This solution is referred to a network that operates at the minimum freshwater consumption of the system. This network has two regeneration processes that treat different flow rates.

Table 9 presents a summary of all the costs and freshwater consumptions for this problem when only the water-using units subsystem is considered, and when it is considered together with the wastewater treatment subsystem. These results will be later analyzed considering the water pretreatment subsystem.

Case 3: Complete Water System. Along with the water-using units data of Table 6, and the wastewater treatment data of Table 7, we use the water pretreatment subsystem data of Table 10, which considers two regeneration processes.

There is one freshwater source that contains 150 ppm of salts, 200 ppm of organics, 3 ppm of H$_2$S and 2 ppm of ammonia. The connection costs applied here are the same ones presented in Table 8. Connections between freshwater source and pretreatments and between pretreatments are not considered. The cost for the connection between pretreatments and any other processes (water-using units and wastewater treatments) are assumed to be the same as the ones from freshwater source and these other processes as presented in Table 8.

If this problem is solved considering an implicit freshwater source with 0 ppm for all the contaminants (that is, a total water system—no recycles to water pretreatment is allowed), the best found solution has a TAC of $1,467,640. This network is the same presented in Figure F33, but now it includes the water pretreatment subsystem and the costs associated with it.

If we still consider only one quality of water (free of contaminants), but we have an explicit water pretreatment subsystem (that is, the whole water pretreatment subsystem is part of the model and thus recycling to the WPT is allowed), we are able to achieve a TAC of $1,422,786. This solution
is presented in Figure 34. Note that not only the TAC is lower, but the freshwater consumption is also reduced to 31,256 t/h.

Additionally, we also can assume the different water pretreatments as individual regeneration process to which recycling can take place. When this case was analyzed, the optimum found solution was the same as the one found in the previous case, where the recycles are allowed and the pretreatments were not individually considered. In fact, the previous solution is a special case and the found solutions indicate that, for this set of cost data, there is no advantage on considering individual water pretreatments instead of considering the water pretreatment subsystem as a “black box.” Example 3 had shown a different situation in which assuming individual water pretreatment rendered advantages to the complete water system. We will later show that a few changes in cost data may show advantages on considering individual water pretreatment.

Moreover, the system presented in Example 5 is able to achieve zero discharge when consumption is minimized. However, zero discharge cycles are not always wanted from the cost point of view. Figure 35 shows the best solution found for a zero discharge option of this system when TAC is minimized. This network has a TAC of $2,526,620. In this network, water from WPT 2, which is free of contaminants, is used to dilute the water from the EoPT with the

Table 9. Costs and Freshwater Consumption Comparison of the Different Options in which only Water-Using Subsystem is Considered or Water-Using and Wastewater Subsystems are Simultaneously Considered

<table>
<thead>
<tr>
<th>System</th>
<th>Recycle of EoPT</th>
<th>TAC ($/year)</th>
<th>Freshwater Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-using Subsystem only</td>
<td>No</td>
<td>$2,291,652</td>
<td>119.332 t/h</td>
</tr>
<tr>
<td>Centralized sequential WWT subsystem at minimum consumption (WUU-WWT)</td>
<td>No</td>
<td>$2,065,383</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Water-using Subsystem only</td>
<td>Yes</td>
<td>$2,062,797</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Centralized distributed WWT subsystem at minimum consumption (WUU-WWT)</td>
<td>No</td>
<td>$1,476,784</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Centralized sequential WWT subsystem (WUU-WWT)</td>
<td>No</td>
<td>$1,351,259</td>
<td>38.983 t/h</td>
</tr>
<tr>
<td>Centralized distributed WWT subsystem (WUU-WWT)</td>
<td>Yes</td>
<td>$1,292,425</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Centralized sequential WWT subsystem* (WUU-WWT)</td>
<td>Yes</td>
<td>$1,292,425</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Integrated Water System at minimum consumption (WUU-WWT)</td>
<td>No</td>
<td>$1,093,011</td>
<td>38.876 t/h</td>
</tr>
<tr>
<td>Integrated Water System (WUU-WWT)</td>
<td>No</td>
<td>$1,065,451</td>
<td>33.571 t/h</td>
</tr>
</tbody>
</table>

Table 10. Data for the Water Pre-Treatment Subsystem

<table>
<thead>
<tr>
<th>CR\textsuperscript{in, max} (ppm)</th>
<th>CR\textsuperscript{out} (ppm)</th>
<th>Capital Cost ($/t\textsuperscript{0.7})</th>
<th>Operating Cost ($/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts</td>
<td>2000</td>
<td>10</td>
<td>$10,000</td>
</tr>
<tr>
<td>Organics</td>
<td>2000</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>500</td>
<td>N/A</td>
<td>$25,300</td>
</tr>
<tr>
<td>Ammonia</td>
<td>1000</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Pre-Treatment 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salts</td>
<td>10</td>
<td>0</td>
<td>$10,000</td>
</tr>
<tr>
<td>Organics</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>5</td>
<td>0</td>
<td>$25,300</td>
</tr>
<tr>
<td>Ammonia</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

WUU-WWT: Case 2 - Interaction between Water-using and Wastewater Treatment Subsystems.

*Same solution was fond either forcing or not the minimum freshwater consumption.

Example 3 had shown a different situation in which assuming individual water pretreatment rendered advantages to the complete water system. We will later show that a few changes in cost data may show advantages on considering individual water pretreatment.

Moreover, the system presented in Example 5 is able to achieve zero discharge when consumption is minimized. However, zero discharge cycles are not always wanted from the cost point of view. Figure 35 shows the best solution found for a zero discharge option of this system when TAC is minimized. This network has a TAC of $2,526,620. In this network, water from WPT 2, which is free of contaminants, is used to dilute the water from the EoPT with the
purpose of bringing the concentration of this mixing down to the maximum allowed inlet concentration in WPT1.

Notice that because self-recycle is not allowed, the dilution happens before WPT 1. In reality, this dilution is necessary to bring the ammonia concentration of the other stream (EoPT) from 30 ppm down to 5 ppm, which is the maximum concentration allowed in WPT 2. To eliminate this issue, we also investigate the case in which self-recycle of regeneration processes, as well as pretreatment processes are allowed. The network correspondent to the best found solution is presented in Figure 36, which has self-recycle in both WPT 1 and WPT 2.

Table 11 presents a summary of all the costs and freshwater consumptions for this problem considering the water pretreatment costs (even if they were not included in the model). Thus, for the networks presented in Table 9, the extra cost with water pretreatment to have freshwater free of contaminants was added.

As previously discussed, we want to show that depending on the costs, a split up of the water pretreatment subsystem in individual water pretreatments, allowing recycles to each of them individually and allowing self-recycles can be advantageous. Here the only data we changed was the freshwater cost. Instead of considering a cost of $0.32/t, we assume that water is free. In this case, which one can encounter sometimes, the best found solution indicates the use of the intermediate water quality from WPT 1. This network is presented in Figure 37. Note that now WPT 1 send water to water-using unit 4.

Conclusions

This article has discussed some of the different structures used to model the water allocation problem. These structures vary according to the different assumption used in each of the subsystems as well as with the interaction among the subsystems. We have shown through examples that different
Figure 36. Grassroots network design for Example 5—Integrated Case with pretreatment—minimum TAC at zero liquid discharge—self-recycle on regeneration and pretreatment allowed.

Table 11. Costs and Freshwater Consumption Comparison of the Different Options—Considering the Complete Water System

<table>
<thead>
<tr>
<th>System</th>
<th>Recycle of EsPT</th>
<th>TAC** ($/year)</th>
<th>Freshwater Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-using Subsystem only</td>
<td>No</td>
<td>$3,674,818</td>
<td>119.332 t/h</td>
</tr>
<tr>
<td>Complete Water System (Zero Liquid Discharge)</td>
<td>Yes</td>
<td>$2,526,620</td>
<td>0 t/h</td>
</tr>
<tr>
<td>Centralized sequential WWT subsystem at minimum consumption (WUU-WWT)</td>
<td>No</td>
<td>$2,467,571</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Centralized distributed WWT subsystem at minimum consumption (WUU-WWT)</td>
<td>No</td>
<td>$1,878,971</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Centralized sequential WWT subsystem (WUU-WWT)</td>
<td>No</td>
<td>$1,816,182</td>
<td>38.983 t/h</td>
</tr>
<tr>
<td>Centralized distributed WWT subsystem (WUU-WWT)</td>
<td>No</td>
<td>$1,795,064</td>
<td>38.983 t/h</td>
</tr>
<tr>
<td>Centralized sequential WWT subsystem* (WUU-WWT)</td>
<td>Yes</td>
<td>$1,694,613</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Centralized distributed WWT subsystem* (WUU-WWT)</td>
<td>Yes</td>
<td>$1,556,695</td>
<td>38.876 t/h</td>
</tr>
<tr>
<td>Integrated Water System (WUU-WWT)</td>
<td>No</td>
<td>$1,526,146</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Integrated Water System at minimum consumption (WUU-WWT)</td>
<td>Yes</td>
<td>$1,467,640</td>
<td>33.571 t/h</td>
</tr>
<tr>
<td>Complete Water System</td>
<td>Yes</td>
<td>$1,422,786</td>
<td>31.256 t/h</td>
</tr>
<tr>
<td>Complete Water System (one water quality)</td>
<td>Yes</td>
<td>$1,422,786</td>
<td>31.256 t/h</td>
</tr>
</tbody>
</table>

WUU-WWT : Case 2 - Interaction between Water-using and Wastewater Treatment Subsystems.

*The same solution was found either forcing or not the minimum freshwater consumption.

*Considering the costs for the Complete Water System.

Figure 37. Grassroots network design for Example 5—integrated case that uses more than one pretreatment water quality.
structural choices can make significant changes. Additionally, we have suggested the inclusion of one more subsystem, the water pretreatment subsystem, to form a complete water system.

In essence, we conclude that when the proper architecture is used, i.e., all subsystem and all recycles among these subsystems are allowed, then the boundaries among these subsystems can be erased, reducing the problem to one big superstructure where all connections are allowed. This is, in many instances, an essential route to achieve zero liquid discharge cycles.

Notation

Sets

\[ w = \text{freshwater sources} \]
\[ u = \text{water-using units} \]
\[ r = \text{regeneration processes (from water pretreatment and/or from wastewater treatment)} \]
\[ s = \text{sinks (or disposal)} \]
\[ c = \text{contaminants} \]

Parameters

\[ CW_{w,c} = \text{concentration of contaminant } c \text{ in the freshwater source } w \]
\[ M_{w,c} = \text{mass load of contaminant } c \text{ extracted in unit } u \]
\[ C_{w,c} = \text{maximum allowed concentration of contaminant } c \text{ at the inlet of unit } u \]
\[ C_{w,c}^{\text{max}} = \text{maximum allowed concentration of contaminant } c \text{ at the outlet of unit } u \]
\[ CRF_{t}^{\text{out}} = \text{outlet concentration of contaminant } c \text{ treated in regeneration process } r \]
\[ XCR_{u,c} = \text{binary parameter that indicates if contaminant } c \text{ is treated by regeneration process } r \]
\[ CR_{u,c}^{\text{max}} = \text{maximum concentration of contaminant } c \text{ allowed at the inlet of regeneration process } r \]
\[ C_{u,c}^{\text{discharge,max}} = \text{maximum allowed concentration at sink } s \]
\[ X_{w} = \text{cost of freshwater } w \]
\[ OP_{u} = \text{operational cost of the regeneration process } r \]
\[ OP = \text{hours of operation per year} \]
\[ af = \text{factor that annualizes the capital cost} \]
\[ CCWU_{w,u} = \text{cost of the connection between freshwater source } w \text{ and water-using unit } u \]
\[ CCWR_{u,c} = \text{cost of the connection between freshwater source } w \text{ and regeneration process } r \]
\[ CCU_{w,u}^{*} = \text{cost of the connection between water-using unit } u \text{ and the water-using unit } u^{*} \]
\[ CCUs_{u,c} = \text{cost of the connection between water-using unit } u \text{ and sink } s \]
\[ CCUR_{u,c} = \text{cost of the connection between water-using unit } u \text{ and regeneration process } r \]
\[ CCRU_{u,c} = \text{cost of the connection between regeneration process } r \text{ and water-using unit } u \]
\[ CCR_{u,c} = \text{cost of the connection between regeneration process } r \text{ and regeneration process } r^{*} \]
\[ CCRS_{u,c} = \text{cost of the connection between regeneration process } r \text{ and sink } s \]
\[ CCR_{t} = \text{cost factor of regeneration process } r \]

Variables

\[ FWU_{w,c} = \text{flow rate from freshwater source } w \text{ to the unit } u \]
\[ FUS_{u,c}^{*} = \text{flow rates between units } u^{*} \text{ and } u \]
\[ FRU_{r,c} = \text{flow rate from regeneration process } r \text{ to unit } u \]
\[ FUS_{u,c} = \text{flow rate from unit } u \text{ to regeneration process } r \]
\[ FRW_{w,c} = \text{flow rate from freshwater source } w \text{ to the regeneration process } r \]
\[ FRR_{r,c} = \text{flow rate from regeneration process } r^{*} \text{ to regeneration process } r \]

FRS_{r,s} = \text{flow rate from regeneration process } r \text{ to sink } s

C_{u,c}^{t} = \text{outlet concentration of contaminant } c \text{ in unit } u

CR_{r,c}^{max} = \text{outlet concentration of the not treated contaminant } c \text{ in regeneration process } r

FR = \text{flow rate through regeneration process } r

Volume

\[ YUU_{u,w} = \text{binary variable to indicate if the connection between freshwater source } w \text{ and the unit } u \text{ exists} \]
\[ YFR_{u,c} = \text{binary variable to indicate if the connection between freshwater source } w \text{ and regeneration process } r \text{ exists} \]
\[ YUU_{u,s} = \text{binary variable to indicate if the connection between water-using unit } u \text{ and water-using unit } u^{*} \text{ exists} \]
\[ YUS_{u,s} = \text{binary variable to indicate if the connection between water-using unit } u \text{ and sink } s \text{ exists} \]
\[ YUR_{r,c} = \text{binary variable to indicate if the connection between regeneration process } r \text{ and water-using unit } u \text{ exists} \]
\[ YRS_{r,c} = \text{binary variable to indicate if the connection between regeneration process } r \text{ and regeneration process } r^{*} \text{ exists} \]
\[ YRS_{r,s} = \text{binary variable to indicate if the connection between regeneration process } r \text{ and sink } s \text{ exists} \]

\[ FCI = \text{fixed capital cost} \]
\[ TAC = \text{total annual cost} \]

Literature Cited


Manuscript received Apr. 19, 2009, and revision received May 24, 2009.