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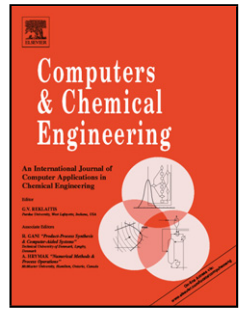

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Synthesis of Water-Using Network with Central Reusable Storage in Batch Processes

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Abstract

The starting and finishing times of water-using operations in batch plants are dependent on the production planning and scheduling. For maximizing the possibility of water reuse/recycle, or for minimizing the freshwater consumption, central storage facilities in a batch water-using system can collect the reusable water from the earlier operations and then supply the remaining water to the later operations. For a predefined production schedule, this paper presents a mathematical formulation for the synthesis of batch water-using networks with central storage tank(s). Superstructures that incorporate all possible flow connections are built to facilitate the problem modeling. The design problem is formulated as a nonlinear program (NLP) if there is no limitation to water reuse/recycle, or a mixed-integer nonlinear program (MINLP) when forbidding water reuse between assigned water-using units and water recycle of certain water-using units is considered. A published literature example and some adaptation examples are provided to demonstrate the good expectation of the proposed, superstructure-based NLP and MINLP formulations.

As supported by the results, superstructures with the design scheme can effectively accomplish the objective of solving the design problem for minimum freshwater consumption and offering the optimal network configuration.

Keywords: Batch process, Synthesis, Water-using network, Superstructure, Nonlinear program (NLP), Mixed-integer nonlinear program (MINLP)

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1 Introduction

Process integration is one of the most important strategies for increasing the overall utilization efficiency of resources and utilities. In contrast with the remarkable advances and extensive applications of heat integration techniques in process industry, only limited investigations on water minimization can be found. Furthermore, most of the methodologies for water minimization in literature are concerning continuous processes. However, because batch operations have become the ordinary works in the production of specialty chemicals of high commercial value, the development of systematic approaches for water minimization in batch plants appeals to academics and practitioners.

It has been shown in literature that adequate arrangements of water reuse/recycle can considerably reduce the total freshwater consumption for water-using systems (Wang & Smith, 1994, 1995a, 1995b). Water reuse concerns the use of outlet water from one water-using unit in another unit, whereas water recycle refers to the use of outlet water from one water-using unit in the same unit. In contrast with their continuous counterpart where the time dimension is completely overridden, the major difficulty in water minimization for batch processes is the inherent time dependence on production planning and scheduling that the operating conditions and freshwater demands are variable with time. Even for a predefined production schedule, the opportunities of water recovery are still constrained by different starting and finishing times of water-using operations.

Wang and Smith (1995b) developed a graphical technique of time pinch analysis for wastewater minimization in batch processes. Both constraints of time and concentration driving force are taken into consideration in their work. In addition, water reuse from the earlier time intervals to the later also indicates the significance of storage facility. Follow-up works on graphical techniques were respectively presented by Foo et al. (2005) and Majozi et al. (2006). However, as pointed out by Majozi (2005a, 2005b), those graphical techniques are only applicable to processes characterized by single contaminants. Majozi (2005a, 2005b, 2006) developed a mathematical formulation to investigate the function of a central reusable water storage facility in bypassing the time limitation for wastewater minimization in batch plants. The formulation can not only be readily extended to multiple contaminant problems, but also used to consider the production scheduling, if necessary. Further studies about the optimal design of water reuse networks in batch processes are also found in literature (Almato et al., 1999; Li & Chang, 2006).

Although water reuse/recycle is effective to reduce the consumption of freshwater in process industries, and the existence of central storage facilities is capable of attenuating the time dependence of batch operations to enhance the opportunities of water recovery, the subject of forbidding water transfers from one water-using unit to another unit is not examined as yet. This paper aims to propose a mathematical formulation to deal with the cases that water reuse between assigned water-using units is forbidden. Three illustrative examples are provided to display the validness of the proposed formulation.

2 Problem Statement

The problem of synthesizing batch water-using network in this paper can be briefly stated as follows. Givens are a set of water-using units $i \in \mathcal{I}$ in which some transferable contaminants $c \in \mathcal{C}$ with fixed mass loads $M_{ic}^{(\text{load})}$ require to be removed and the maximum permissible inlet/outlet concentrations for each unit, $C_{ic,\max}^{(\text{in})}$/$C_{ic,\max}^{(\text{out})}$, are also specified; a set of water sources $w \in \mathcal{W}$ with specific concentrations C_{wc} for utilization, where some of them supply freshwater $w \in \mathcal{F} \subseteq \mathcal{W}$; a set of storage tanks $s \in \mathcal{S}$ for the temporary storage of used water to enhance water recovery. Furthermore, the production scheduling is assumed to be known and the starting and finishing times of water-using operation in each unit have been assigned to their corresponding time points $p \in \mathcal{P}$. The objective is to determine the time-dependent operating strategy which targets the minimum freshwater consumption. The solution of problem provides the minimized freshwater consumption, resultant network configuration and accumulation of used water in storage tanks. It has to be mentioned that the investment costs will not be addressed in this work, even though the adaptability to include economic factors among design criteria is part of the motivation for applying mathematical techniques. To emphasize the impact of available storage tanks on the reduction of freshwater, the investment costs are temporarily left out from the problem

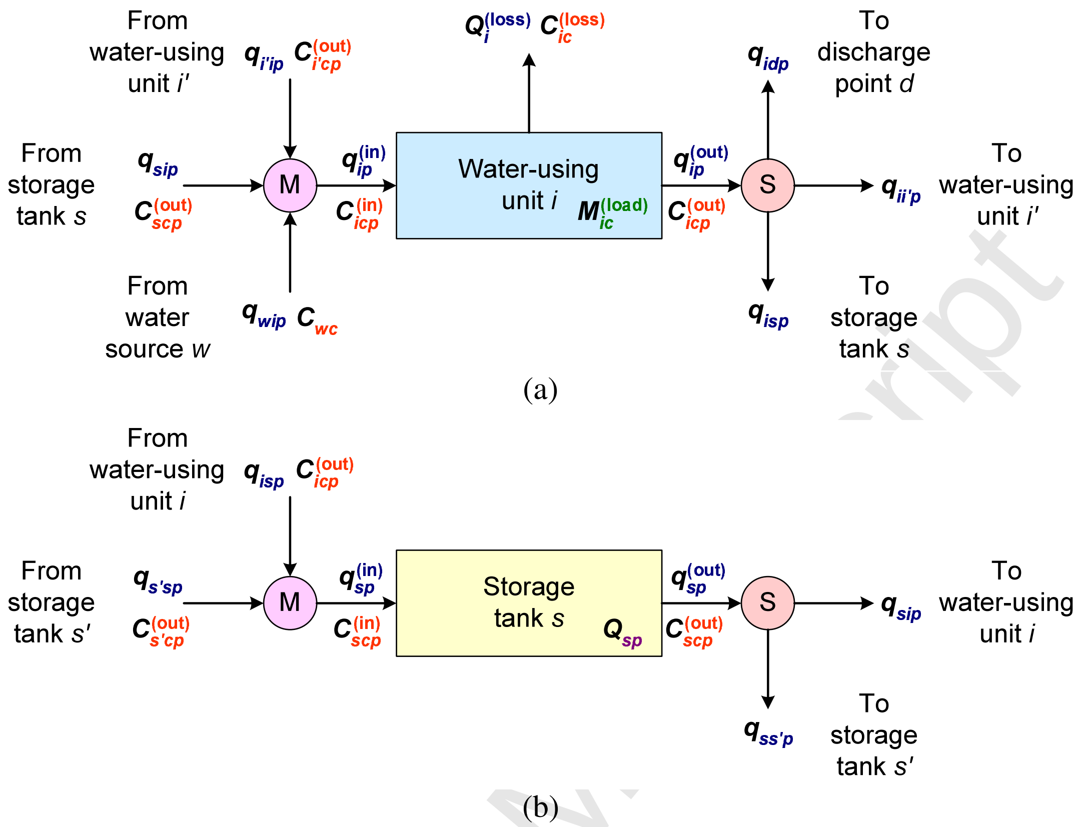

Figure 1: Superstructures for (a) water-using unit and (b) storage tank.

formulation and this issue will be tackled in the future work.

3 Superstructures and Problem Formulation

In order to formulate the synthesis problem, generic superstructures for water-using unit and storage tank are constructed to incorporate all possible flow connections within the batch water system, as shown in Fig.s 1(a) and (b) respectively. The problem formulation presented in the following sections mainly involves water and contaminant balances around each water-using unit and storage tank. All required indices, sets, parameters and variables are marked on Fig. 1 and listed in the table of Nomenclature.

3.1 Water balance around water-using units

The overall water balances toward water-using units are formulated on the basis of the superstructure in Fig. 1(a), including the inlet flow from sources, the outlet flow to sinks and the relation between inlet and outlet flows. For dealing with the time dependence of batch process, two sets of binary parameters, $y_{ip}^{(\text{st.})}$ and $y_{ip}^{(\text{fin.})}$, are predefined to indicate the starting and finishing times of all operations in water-using units. $y_{ip}^{(\text{st.})} = 1$ means that the operation in unit i is starting at time point p, while $y_{ip}^{(\text{fin.})} = 1$ signifies that the operation in unit i is finishing at time point p.

$$q_{ip}^{(\text{in})} = \sum_{\forall i' \in \mathcal{I}} q_{i'ip} + \sum_{\forall s \in \mathcal{S}} q_{sip} + \sum_{\forall w \in \mathcal{W}} q_{wip} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P} \tag{1}$$

$$q_{ip}^{(\text{out})} = \sum_{\forall d \in \mathcal{D}} q_{idp} + \sum_{\forall i' \in \mathcal{I}} q_{ii'p} + \sum_{\forall s \in \mathcal{S}} q_{isp} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P} \tag{2}$$

$$Q_i^{\text{L}} y_{ip}^{(\text{st.})} \leq q_{ip}^{(\text{in})} \leq Q_i^{\text{U}} y_{ip}^{(\text{st.})} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P} \tag{3}$$

$$Q_i^{\text{L}} y_{ip}^{(\text{fin.})} \leq q_{ip}^{(\text{out})} \leq Q_i^{\text{U}} y_{ip}^{(\text{fin.})} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P} \tag{4}$$

$$q_{ip}^{(\text{in})} - q_{i,p+\Delta_i}^{(\text{out})} - y_{ip}^{(\text{in})} Q_i^{(\text{loss})} = 0 \qquad \forall i \in \mathcal{I}, p \in \mathcal{P} \tag{5}$$

Equations (1) and (2) are water balances around mixing point M and splitting point S of unit i at time point p. Equations (3) and (4) give lower and upper bounds for the inlet and outlet flows of unit i at time point p. The amount of water entering and leaving unit i at time point p will be bounded in a reasonable range if the operation is about to start or finished at that time point. On the other hand, those two equations also ensure that no water flows in and out when the time point is neither a starting nor finishing time for the operation. Equation (5) is the water balance throughout unit i, where the amount of water loss during operation is assumed to be a known constant or function. Note that Δ_i is the distance between time points for the starting and finishing of the operation in unit i, which reflects a certain duration to achieve the expected effect.

3.2 Contaminant balance around water-using units

As stated in the following, Eq. (6) is the contaminant balance around the mixing point before unit i at time point p. Equation (7) is the contaminant balance throughout unit i, in which the concentration of water loss is assumed to be a known parameter. Equation (8) gives the maximum permissible inlet and outlet concentrations of contaminant c for unit i as the constraints on concentration driving force. Besides, it should be realized that the outlet flow is always prior to the inlet flow when a water-using operation is finishing and starting immediately at the same time point.

$$q_{ip}^{(\text{in})} C_{icp}^{(\text{in})} = \sum_{\forall i' \in \mathcal{I}} q_{i'ip} C_{i'cp}^{(\text{out})} + \sum_{\forall s \in \mathcal{S}} q_{sip} C_{scp}^{(\text{out})} + \sum_{\forall w \in \mathcal{W}} q_{wip} C_{wc} \qquad \forall c \in \mathcal{C}, i \in \mathcal{I}, p \in \mathcal{P} \tag{6}$$

$$q_{ip}^{(\text{in})} C_{icp}^{(\text{in})} - q_{i,p+\Delta_i}^{(\text{out})} C_{ic,p+\Delta_i}^{(\text{out})} + y_{ip}^{(\text{in})} (M_{ic}^{(\text{load})} - Q_i^{(\text{loss})} C_{ic}^{(\text{loss})}) = 0 \qquad \forall c \in \mathcal{C}, i \in \mathcal{I}, p \in \mathcal{P} \tag{7}$$

$$C_{icp}^{(\text{in})} \leq C_{ic,\max}^{(\text{in})}; C_{icp}^{(\text{out})} \leq C_{ic,\max}^{(\text{out})} \qquad \forall c \in \mathcal{C}, i \in \mathcal{I}, p \in \mathcal{P} \tag{8}$$

3.3 Water balance around storage tanks

Based on the superstructure in Fig. 1(b), water balances for storage tanks are similar to those for water-using units, as stated below. Equations (9) and (10) are the water balances around the mixing and splitting points of storage tank s at time point p. Equations (11) and (12) provide the water balance throughout storage tank s to calculate the amount of remaining water therein at time point p. Note that $Z^{(\text{cyc.})}$ is a predefined binary parameter to describe two operating modes. $Z^{(\text{cyc.})} = 0$ denotes the single operation where no initial storage is assumed, and $Z^{(\text{cyc.})} = 1$ indicates the cyclic operation where the initial storage is equivalent to the remaining water at the last time point P for the previous batch cycle. Equation (13) gives an upper bound for the capacity of storage tank s.

$$q_{sp}^{(\text{in})} = \sum_{\forall i \in \mathcal{I}} q_{isp} + \sum_{\forall s' \in \mathcal{S}} q_{s'sp} \qquad \forall p \in \mathcal{P}, s \in \mathcal{S} \tag{9}$$

$$q_{sp}^{(\text{out})} = \sum_{\forall i \in \mathcal{I}} q_{sip} + \sum_{\forall s' \in \mathcal{S}} q_{ss'p} \qquad \forall p \in \mathcal{P}, s \in \mathcal{S} \tag{10}$$

$$Q_{sp} = Q_{s,p-1} + q_{sp}^{(\text{in})} - q_{sp}^{(\text{out})} \qquad \forall p \in \mathcal{P}^*, s \in \mathcal{S} \tag{11}$$

$$Q_{sp} = Z^{(\text{cyc.})} Q_{sP} + q_{sp}^{(\text{in})} - q_{sp}^{(\text{out})} \qquad \forall p = 1, s \in \mathcal{S} \tag{12}$$

$$Q_{sp} \leq Q_s^{\text{U}} \qquad \forall p \in \mathcal{P}, s \in \mathcal{S} \tag{13}$$

3.4 Contaminant balance around storage tanks

The contaminant balances for storage tanks are also formulated as follows. Here, it is assumed that the inlet flow is prior to the outlet flow when there are water flows entering and leaving a storage tank at the same time point. Equation (14) is the contaminant balance around the mixing point of storage tank s at time point p. Moreover, Equations (15) and (16) are the contaminant balance throughout the storage tank s at time point p.

$$q_{sp}^{(\mathrm{in})} C_{scp}^{(\mathrm{in})} = \sum_{\forall i \in \mathcal{I}} q_{isp} C_{icp}^{(\mathrm{out})} + \sum_{\forall s' \in \mathcal{S}} q_{s'sp} C_{s'cp}^{(\mathrm{out})} \qquad \forall c \in \mathcal{C}, p \in \mathcal{P}, s \in \mathcal{S} \tag{14}$$

$$Q_{sp} C_{scp}^{(\mathrm{out})} = Q_{s,p-1} C_{sc,p-1}^{(\mathrm{out})} + q_{sp}^{(\mathrm{in})} C_{scp}^{(\mathrm{in})} - q_{sp}^{(\mathrm{out})} C_{scp}^{(\mathrm{out})} \qquad \forall c \in \mathcal{C}, p \in \mathcal{P}^*, s \in \mathcal{S} \tag{15}$$

$$Q_{sp} C_{scp}^{(\mathrm{out})} = Z^{(\mathrm{cyc.})} Q_{sP} C_{scP}^{(\mathrm{out})} + q_{sp}^{(\mathrm{in})} C_{scp}^{(\mathrm{in})} - q_{sp}^{(\mathrm{out})} C_{scp}^{(\mathrm{out})} \qquad \forall c \in \mathcal{C}, p = 1, s \in \mathcal{S} \tag{16}$$

3.5 Objective functions

The main objective in this work is to minimize the freshwater consumption on water-using operations, and the design problem is formulated as the following nonlinear program (NLP). Note that $\boldsymbol{x}_1$ is the vector of all design variables, and $\boldsymbol{\Omega}_1$ is the feasible searching space delimited by all design constraints.

$$\textbf{P1:} \min_{\boldsymbol{x}_1 \in \boldsymbol{\Omega}_1} J_1 = \sum_{\forall w \in \mathcal{F}} \sum_{\forall i \in \mathcal{I}} \sum_{\forall p \in \mathcal{P}} q_{wip} \tag{17}$$

$$\boldsymbol{x}_1 \equiv \left\{ \begin{array}{c} q_{idp}, q_{ii'p}, q_{isp}, q_{sip}, q_{wip}, q_{ip}^{(\mathrm{in})}, q_{ip}^{(\mathrm{out})} \\ q_{sp}^{(\mathrm{in})}, q_{sp}^{(\mathrm{out})}, Q_{sp}, C_{icp}^{(\mathrm{in})}, C_{icp}^{(\mathrm{out})}, C_{scp}^{(\mathrm{in})}, C_{scp}^{(\mathrm{out})} \\ \forall c \in \mathcal{C}, d \in \mathcal{D}, i, i' \in \mathcal{I}, p \in \mathcal{P}, s \in \mathcal{S}, w \in \mathcal{W} \end{array} \right\} \tag{18}$$

$$\boldsymbol{\Omega}_1 = \{ \boldsymbol{x}_1 \mid \text{Eqs. } (1) - (16) \} \tag{19}$$

Because design problem **P1** may result in multiple solutions in terms of network configuration, one can minimize the overall capacity of storage tanks as the secondary objective to obtain a preferable design, as stated in the following NLP. Note that the maximum capacity of each storage tank $Q_s^{\max}$ is considered as a design variable at this moment, and the searching space is contracted to $\boldsymbol{\Omega}_1'$ with the additional constraint, for maintaining the minimum consumption of freshwater.

$$\textbf{P2:} \min_{\boldsymbol{x}_1' \in \boldsymbol{\Omega}_1'} J_2 = \sum_{\forall s \in \mathcal{S}} Q_s^{\max} \tag{20}$$

$$\boldsymbol{x}_1' \equiv \boldsymbol{x}_1 \cup \{Q_s^{\max},\ \forall s \in \mathcal{S}\} \tag{21}$$

$$\boldsymbol{\Omega}_1' = \boldsymbol{\Omega}_1 \cap \left\{ \boldsymbol{x}_1' \;\middle|\; \begin{array}{l} \sum\limits_{\forall w \in \mathcal{F}} \sum\limits_{\forall i \in \mathcal{I}} \sum\limits_{\forall p \in \mathcal{P}} q_{wip} \leq J_1^* \\ Q_{sp} \leq Q_s^{\max},\ \forall p \in \mathcal{P}, s \in \mathcal{S} \end{array} \right\} \tag{22}$$

4 Illustrative Examples

Three examples are present to illustrate the validness of the proposed formulation for synthesizing batch water-using networks. All mathematical programs are solved by using the General Algebraic Modeling System (GAMS, Brooke et al., 2003) in a Core 2, 2 GHz processor. Moreover, the solver selected for NLP is SNOPT.

4.1 Example 1: five single-stage operations

The first example is taken from Majozi (2005a, 2005b and 2006) regarding the execution of five water-using operations in an agrochemical manufacturing facility: freshwater is introduced to form an aqueous phase for the liquid-liquid extraction to remove sodium chloride from the organic phase. The basic processing data for each operation, including lower and upper bounds for the inlet and outlet water flows, maximum permissible inlet and outlet concentrations, starting and finishing times and contaminant mass load, are all given in Table 1. According to the known schedule, Fig. 2 shows the corresponding Gantt chart of this example. Note that the constant interval between any two time points adopted in the problem formulation is 0.5-h, and therefore, sixteen time points are required over a 7.5-h time horizon. Also note that, for this example, the five water-using operations are included into a single batch operation.

For a start, the mode of single operation without a storage tank is considered. As the resultant network configuration shown in Fig. 3(a), every unit has used freshwater with a total consumption of 1767.84 kg per batch. Part of the outlet water from unit B (D) is reused in unit C (E) after the dilution with freshwater. Nevertheless, the outlet water from unit A is not reused in other units but directly discharged because of the time limitation, although it is at a qualified concentration for all other units. An existing storage tank can temporarily store the outlet water of unit A and then supply it to units C and E for reuse,

Table 1: Processing data for examples 1 and 2.

Unit	$[Q_i^{\min}, Q_i^{\max}]$ (kg)	$C_{ic,\max}^{(\text{in})}$ (kg salt/kg water)	$C_{ic,\max}^{(\text{out})}$	$t_{ip}^{(\text{st.})}$ (h)	$t_{ip}^{(\text{fin.})}$ (h)	$M_{ic}^{(\text{load})}$ (kg)
A	$[0, 1000]$	0	0.1	0	3 (Example 1) 4.5 (Example 2)	100
B	$[0, 280]$	0.25	0.51	0	4	72.8
C	$[300, 400]$	0.1	0.1	4	5.5	0
D	$[0, 280]$	0.25	0.51	2	6	72.8
E	$[300, 400]$	0.1	0.1	6	7.5	0

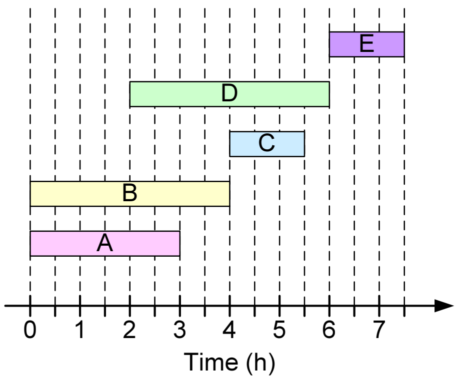

Figure 2: Gantt chart for the production schedule of example 1.

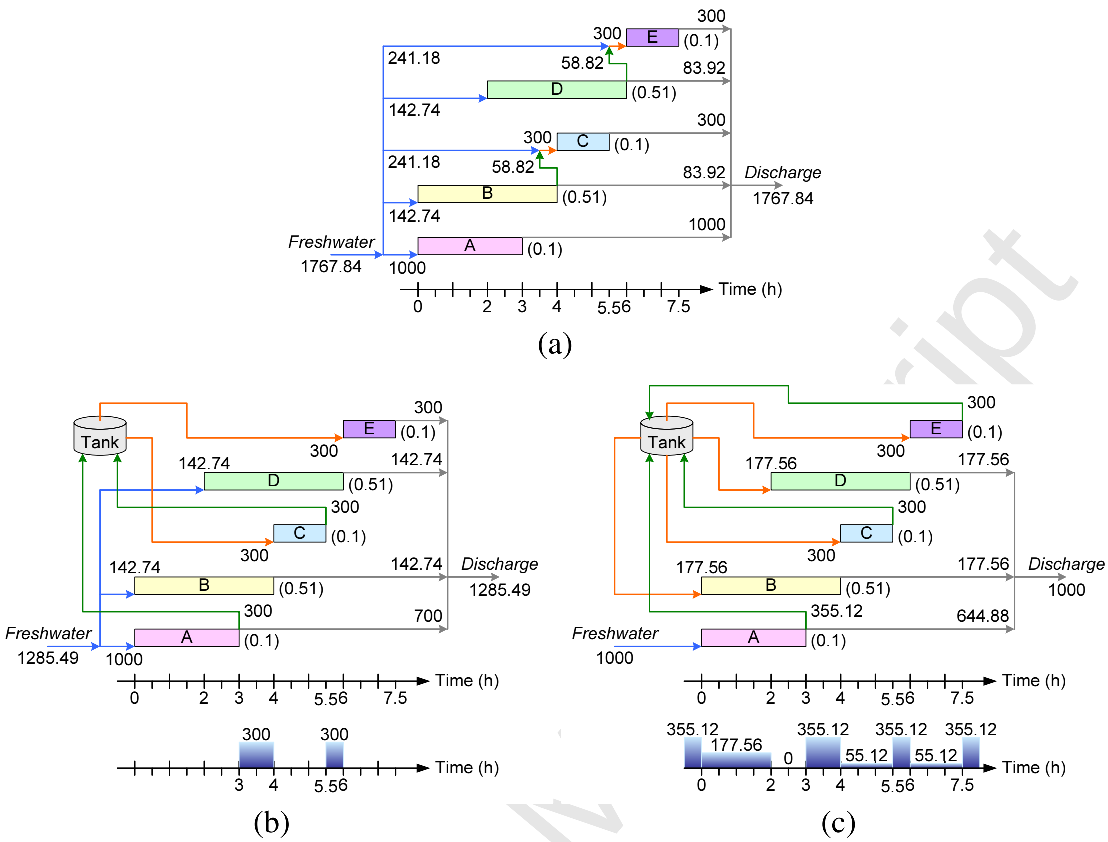

Figure 3: Resultant networks of example 1: (a) single operation without a storage tank, (b) single operation with one storage tank, and (c) cyclic operation with one storage tank.

as shown in Fig. 3(b). Consequently, the freshwater consumption for single operation is decreased from 1767.84 kg to 1285.49 kg (per batch) with the existence of storage tank. Moreover, the required capacity of storage tank is 300 kg, and the storage profile is also shown in Fig. 3(b). Because of the fact that the outlet water of units C and E can be stored and reused by units B and D in the next batch operation, the mode of cyclic operation will further reduce the freshwater consumption from 1285.49 kg to 1000 kg (per batch), with a slight increase of storage capacity from 300 kg to 355.12 kg, as shown in Fig. 3(c). All computation results, including problem structure, the number of variables, the number of constraints and CPU time, are summarized in Table 2.

4.2 Example 2: modified case with longer operating time

The second example is a modification of example 1 where the operating time of unit A is extended to 4.5 hours, as shown in Table 1. The freshwater consumptions for single

Table 2: Computation results of examples 1 and 2.

Operating mode		Single op.		Cyclic op.
No. of storage tanks		0	1	
Problem structure		**NLP**		
No. of constraints		881	977	977
Continuous variables		881	1121	1121
Ex. 1	Freshwater (kg)	1767.84	1285.49	1000
	Storage cap. (kg)	0	300	355.12
	CPU time (sec)	0.17	0.20	0.22
Ex. 2	Freshwater (kg)	1767.84	1526.67	1000
	Storage cap. (kg)	0	300	655.12
	CPU time (sec)	0.19	0.20	0.22

operation without and with one storage tank are 1767.84 kg and 1526.67 kg (per batch), respectively, while the freshwater consumption for cyclic operation with one storage tank is 1000 kg per batch. The resultant network configurations of this example are similar to those of the previous one, as shown in Fig.s 4(a)-(c). Furthermore, the required capacities of storage tanks for single and cyclic operations are 300 kg and 655.122 kg, respectively. All computation results of example 2 are also summarized in Table 2.

4.3 Forbidden water reuse/recycle

It is quite common that the water reuse between certain water-using units is forbidden for antipollution. In other words, the feasibility of water reuse from one water-using unit to another is dependent on not only the concentration constraint but also the operational consideration. Until now, only a few works in literature have addressed forbidden matches for continuous processes using mathematical formulation (Bagajewicz & Savelski, 2001; Gunaratnam et al., 2005), but there is no parallel information for batch processes.

Review the previous two examples and suppose that the water reuse between units C and E is forbidden, and what's more, the water recycle of units C and E is also prohibited. Accordingly, some of the resultant networks should be changed to satisfy the operational constraints. As observed in both Fig.s 3(b) and (c), the original designs of example 1 for single and cyclic operations each with one storage tank, the reuse of water from unit C to unit E is undesired. Besides, as the original design of example 2 for cyclic operation with

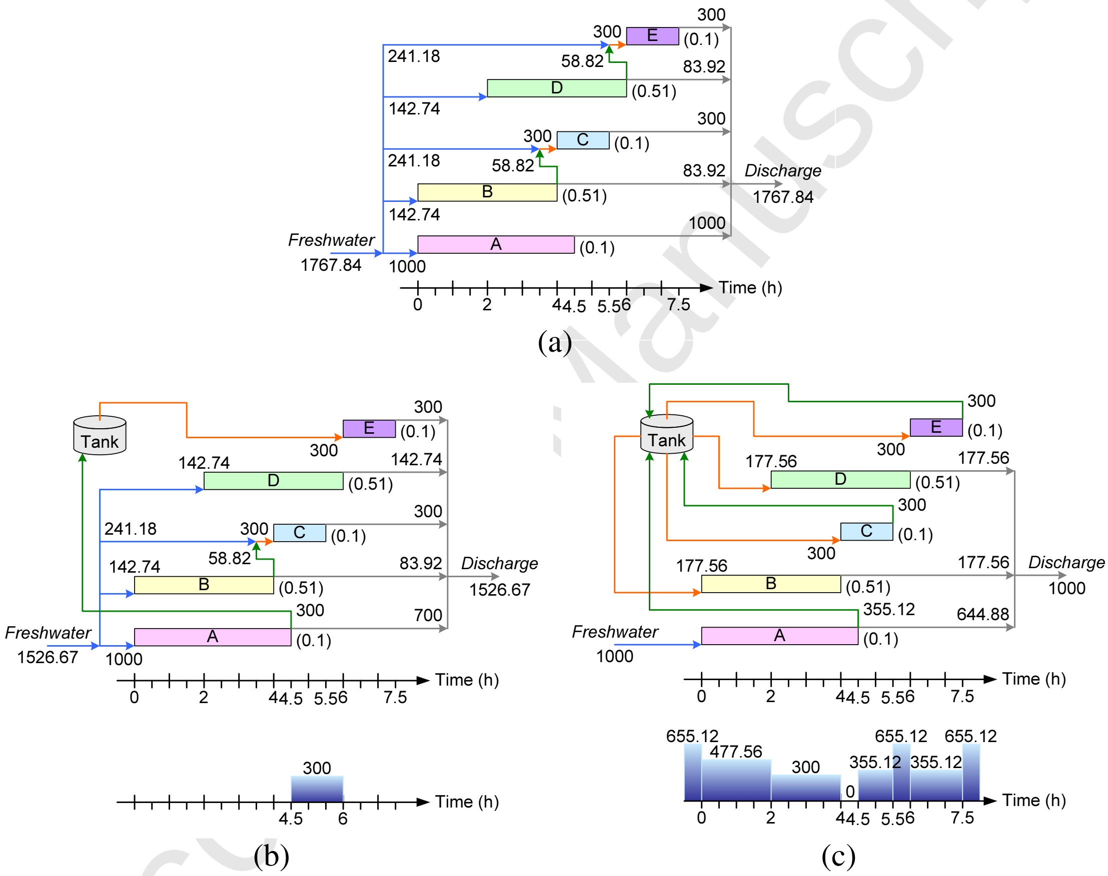

Figure 4: Resultant networks of example 2: (a) single operation without a storage tank, (b) single operation with one storage tank, and (c) cyclic operation with one storage tank.

one storage tank shown in Fig. 4(c), the water reuse from unit C to unit E, from unit E to unit C, and the water recycle of unit C are all undesired.

4.3.1 Logical constraints for forbidding water reuse/recycle

To achieve practical designs without the forbidden water reuse/recycle, some relevant binary variables and constraints must be added into the problem formulation. Firstly, a set of binary variables $Z_{ii'p}$, Z_{isp} and Z_{sip} are introduced to indicate the existence of "direct" connections. The following expressions, Eqs. (23)-(25), are used to correlate the binary variables with the continuous variables. For instance, $Z_{ii'p} = 1$ indicates the existence of connecting flow from unit i to another unit i' at time point p, with the amount positioned between a pair of reasonable lower and upper bounds.

$$Q^{\mathrm{L}}_{ii'} Z_{ii'p} \leq q_{ii'p} \leq Q^{\mathrm{U}}_{ii'} Z_{ii'p} \qquad \forall i, i' \in \mathcal{I}, p \in \mathcal{P} \tag{23}$$

$$Q^{\mathrm{L}}_{is} Z_{isp} \leq q_{isp} \leq Q^{\mathrm{U}}_{is} Z_{isp} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P}, s \in \mathcal{S} \tag{24}$$

$$Q^{\mathrm{L}}_{si} Z_{sip} \leq q_{sip} \leq Q^{\mathrm{U}}_{si} Z_{sip} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P}, s \in \mathcal{S} \tag{25}$$

In addition to the direct connections, the existence of "indirect" connections has to be identified because of the fact that water transfers between water-using units and/or storage tanks will be also in a circuitous way. For example, the outlet water from one water-using unit to another may pass through other units or storage tanks on the way. For this reason, another set of binary variables $X_{ii'p}$, X_{isp} and X_{sip} are further introduced to include such indirect connections: $X_{ii'p} = 1$ represents that unit i' has received the water from unit i at time point p in direct or indirect ways; $X_{isp} = 1$ denotes that storage tank s has received the water from unit i at time point p in direct or indirect ways, whereas $X_{sip} = 1$ signifies that unit i has received the water from storage tank s at time point p in direct or indirect ways. In order to make an adaptation of the current situation as well as for the purpose of simplification, only one storage tank is considered in the design system, for the moment.

Logical relations between direct and indirect connections are presented as follows.

$$X_{ii'p} \geq Z_{ii'p} \qquad \forall i, i' \in \mathcal{I}, p \in \mathcal{P} \tag{26}$$

$$X_{ii'p} \geq X_{ii'',p-\Delta_{i''}} Z_{i''i'p} \qquad \forall i, i', i'' \in \mathcal{I}, p \in \mathcal{P}, p > \Delta_{i''} \tag{27}$$

$$X_{ii'p} \leq Z_{ii'p} + \sum_{\forall i'' \in \mathcal{I}} (X_{ii'',p-\Delta_{i''}} Z_{i''i'p})\Big|_{p>\Delta_{i''}} \qquad \forall i, i' \in \mathcal{I}, p \in \mathcal{P} \tag{28}$$

Equations (26) and (27) state that unit i' will be recognized as receiving the water from unit i at time point p if there exist direct flow from unit i or indirect flow through unit i''. Equation (28) ensures that no water from unit i has been received by unit i' at time point p if there is neither direct nor indirect connection. It is important to note that any possible paths of water transfers included in $X_{ii'p}$ are not involved the storage tank.

$$X_{isp} \geq Z_{isp} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P}, s \in \mathcal{S} \tag{29}$$

$$X_{isp} \geq X_{ii',p-\Delta_{i'}} Z_{i'sp} \qquad \forall i, i' \in \mathcal{I}, p \in \mathcal{P}, p > \Delta_{i'}, s \in \mathcal{S} \tag{30}$$

$$X_{isp} \leq Z_{isp} + \sum_{\forall i' \in \mathcal{I}} (X_{ii',p-\Delta_{i'}} Z_{i'sp})\Big|_{p>\Delta_{i'}} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P}, s \in \mathcal{S} \tag{31}$$

Equations (29) and (30) state that storage tank s will be recognized to receive the water from unit i at time point p if there exist direct flow from unit i or indirect flow via unit i'. Note that the circuitous way from one water-using unit to storage tank is simply passing through other units for the situation of single storage tank. Equation (31) ensures that no water from unit i has been received by storage tank s at time point p providing there exists no direct nor indirect connection.

$$X_{sip} \geq Z_{sip} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P}, s \in \mathcal{S} \tag{32}$$

$$X_{sip} \geq X_{si',p-\Delta_{i'}} Z_{i'ip} \qquad \forall i, i' \in \mathcal{I}, p \in \mathcal{P}, p > \Delta_{i'}, s \in \mathcal{S} \tag{33}$$

$$X_{sip} \leq Z_{sip} + \sum_{\forall i' \in \mathcal{I}} (X_{si',p-\Delta_{i'}} Z_{i'ip})\Big|_{p>\Delta_{i'}} \qquad \forall i \in \mathcal{I}, p \in \mathcal{P}, s \in \mathcal{S} \tag{34}$$

Similarly, Eqs. (32) and (33) express that unit i will be recognized to receive the water from storage tank s at time point p if there exists direct flow from storage tank s or indirect flow via unit i'. Equation (34) ensures that no water from storage tank s has been received by unit i at time point p in case no direct nor indirect connection occurs.

Apart from the identification of all flow connections, the condition inside the storage tank is also considerable and binary variables $Y_{sp}^{(\mathrm{occ.})}$ and $E_{spp'}$ are defined accordingly. As presented in Eq. (35), $Y_{sp}^{(\mathrm{occ.})} = 1$ denotes that storage tank s keeps a finite storage at time point p, on the other hand, $Y_{sp}^{(\mathrm{occ.})} = 0$ reflects that the storage tank is empty.

$$Q_s^{\mathrm{L}} Y_{sp}^{(\mathrm{occ.})} \leq Q_{sp} \leq Q_s^{\mathrm{U}} Y_{sp}^{(\mathrm{occ.})} \qquad \forall p \in \mathcal{P}, s \in \mathcal{S} \tag{35}$$

Furthermore, Eqs. (36) and (37) are used to examine the internal condition of storage tank s during a particular time period. It is obviously that storage tank s will be recognized to have been emptied during the time period from p to p' ($E_{spp'} = 1$) if there is no storage remaining in storage tank s for at least one time point $p'' \in [p, p']$.

$$E_{spp'} \geq 1 - Y_{sp''}^{(\mathrm{occ.})} \qquad \forall p, p', p'' \in \mathcal{P}, p \leq p'' \leq p', s \in \mathcal{S} \tag{36}$$

$$E_{spp'} \leq \sum_{p'' \in [p,p']} (1 - Y_{sp''}^{(\mathrm{occ.})}) \qquad \forall p, p' \in \mathcal{P}, s \in \mathcal{S} \tag{37}$$

On the basis of the above binary variables and logical expressions, the forbidden water reuse/recycle can be avoided by imposing the following constraints. It is clear as depicted in Eq. (38) that $X_{ii'p}$ is forced to be zero to prohibit the water transfer from unit i to unit i' directly or via other units. Note that $\mathcal{I}^{\mathrm{forbid}}$ is an assigned set of forbidden unit pairs, in which both forbidden water reuse ($i \neq i'$) and recycle ($i = i'$) are covered, $\forall i, i' \in \mathcal{I}$.

$$X_{ii'p} = 0 \qquad \forall (i, i') \in \mathcal{I}^{\mathrm{forbid}}, p \in \mathcal{P} \tag{38}$$

Equations (39)-(41) are used in another case for water transfers involving the storage tank, where the receivability of water from storage tank s to unit i is examined. Definitely, for the prohibition of water transfer from unit i to unit i', unit i' cannot receive any water from storage tank s after unit i supplying water to the storage tank, until the water stored in storage tank s has been emptied by other units. In other words, as described in Eq. (39), if storage tank s has received the water from unit i at an earlier time point p' ($X_{isp'} = 1$) and keeps a certain amount of storage all the time during the time period from p' to $p - 1$ ($E_{sp',p-1} = 0$), unit i' cannot receive any water from storage tank s at time point p ($X_{si'p}$ will be forced to be zero). Moreover, as described in Eq. (40), if storage tank s has received the water from unit i at a later time point p' in the time scale and keeps the storage without being emptied, past the current batch and continued to an earlier time point $p-1$ in next batch ($E_{sp'P}=0$ and $E_{s1,p-1}=0$), unit i' cannot receive the water from storage tank s at time point p. Equation (41) is specially for the first time point $p=1$, where the condition in the previous batch cycle is referred when cyclic operation.

$$X_{si'p} \leq 1 - X_{isp'} + E_{sp',p-1} \quad \forall (i,i') \in \mathcal{I}^{\text{forbid}}, p, p' \in \mathcal{P}, p > p', s \in \mathcal{S} \tag{39}$$

$$X_{si'p} \leq 1 - (X_{isp'} - E_{sp'P} - E_{s1,p-1}) Z^{(\text{cyc.})} \quad \forall (i,i') \in \mathcal{I}^{\text{forbid}}, p, p' \in \mathcal{P}^*, p \leq p', s \in \mathcal{S} \tag{40}$$

$$X_{si'p} \leq 1 - (X_{isp'} - E_{sp'P}) Z^{(\text{cyc.})} \quad \forall (i,i') \in \mathcal{I}^{\text{forbid}}, p = 1, p' \in \mathcal{P}, s \in \mathcal{S} \tag{41}$$

4.3.2 Practical design excluding forbidden water reuse/recycle

Revisit examples 1 and 2 with the additional binary variables and logical constraints. For the same objective to minimize the consumption of freshwater, the design problem is formulated as the following mixed-integer nonlinear program (MINLP).

$$\textbf{P3:} \min_{\boldsymbol{x}_2 \in \boldsymbol{\Omega}_2} J_3 = \sum_{\forall w \in \mathcal{F}} \sum_{\forall i \in \mathcal{I}} \sum_{\forall p \in \mathcal{P}} q_{wip} \tag{42}$$

$$\boldsymbol{x}_2 \equiv \boldsymbol{x}_1 \cup \left\{ \begin{array}{c} Z_{ii'p}, Z_{isp}, Z_{sip}, X_{ii'p} \\ X_{isp}, X_{sip}, Y_{sp}^{(\text{occ.})}, E_{spp'} \\ \forall i, i' \in \mathcal{I}, p, p' \in \mathcal{P}, s \in \mathcal{S} \end{array} \right\} \tag{43}$$

$$\boldsymbol{\Omega}_2 = \boldsymbol{\Omega}_1 \cap \{\boldsymbol{x}_2 \,|\, \text{Eqs. } (23) - (41)\} \tag{44}$$

To reduce multiple solutions for a more applicable network configuration, the minimization of storage capacity is further considered.

$$\textbf{P4:} \min_{\boldsymbol{x}'_2 \in \boldsymbol{\Omega}'_2} J_4 = \sum_{\forall s \in \mathcal{S}} Q_s^{\max} \tag{45}$$

$$\boldsymbol{x}'_2 \equiv \boldsymbol{x}_2 \cup \{Q_s^{\max},\ \forall s \in \mathcal{S}\} \tag{46}$$

$$\boldsymbol{\Omega}'_2 = \boldsymbol{\Omega}_2 \cap \left\{ \boldsymbol{x}'_2 \left| \begin{array}{l} \sum_{\forall w \in \mathcal{F}} \sum_{\forall i \in \mathcal{I}} \sum_{\forall p \in \mathcal{P}} q_{wip} \leq J_3^* \\ Q_{sp} \leq Q_s^{\max},\ \forall p \in \mathcal{P}, s \in \mathcal{S} \end{array} \right. \right\} \tag{47}$$

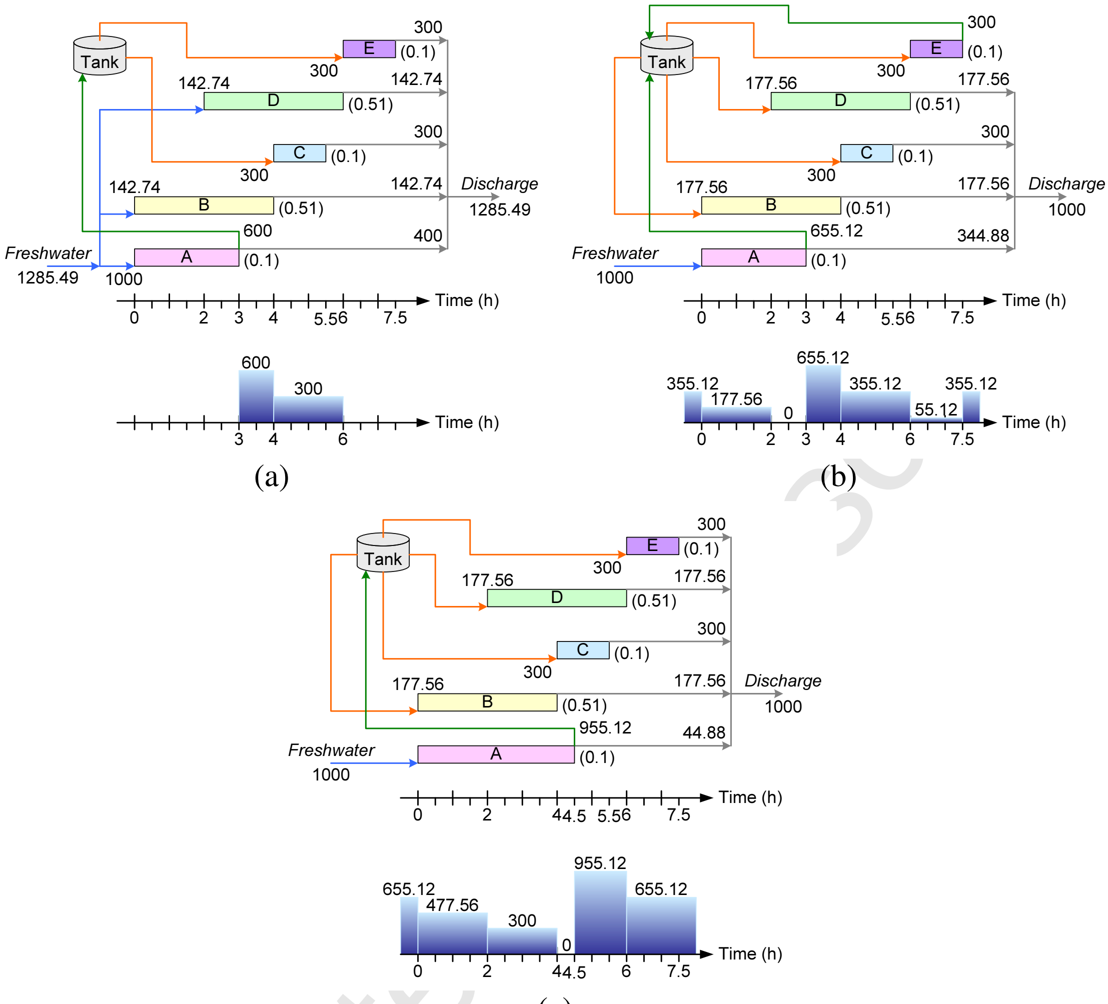

Figure 5: Revised networks after forbidding water reuse/recycle in units C and E: (a) single and (b) cyclic operation with one storage tank for example 1, and (c) cyclic operation with one storage tank for example 2.

A set of forbidden unit pairs $\mathcal{I}^{\text{forbid}} = \{(\text{C}, \text{E}), (\text{E}, \text{C}), (\text{C}, \text{C}), (\text{E}, \text{E})\}$ is assigned here for the cases of single and cyclic operations in example 1, and cyclic operation in example 2. As the revised networks of example 1 shown in Fig.s 5(a) and (b), the outlet water from unit C is discharged instead of entering the storage tank. Besides, the revised network for example 2 in Fig. 5(c) shows that the outlet water from both units C and E is discharged rather than being stored. The freshwater consumptions for those cases are kept the same (1285.49 kg, 1000 kg and 1000 kg) at the expense of the enlarged storage capacities (600 kg, 655.12 kg and 955.12 kg). The solver selected for MINLP is SBB, and all computation results are summarized in Table 3.

Table 3: Computation results of cases with forbidden reuse/recycle.

Case	Example 1		Example 2
Operating mode	Single op.	Cyclic op.	Cyclic op.
Problem structure	**MINLP**		
No. of constraints	6294	7230	7125
Continuous variables	1121	1121	1121
Discrete variables	1392	1392	1392
Freshwater (kg)	1285.49	1000	1000
Storage cap. (kg)	600	655.12	955.12
CPU time (sec)	2.14	5.25	6.06

Table 4: Processing data for example 3.

Unit	$[Q_i^{\min}, Q_i^{\max}]$ (kg)	$C_{ic,\max}^{(\text{in})}$ (kg salt/kg water)	$C_{ic,\max}^{(\text{out})}$	$t_{ip}^{(\text{st.})}$ (h)	$t_{ip}^{(\text{fin.})}$ (h)	$M_{ic}^{(\text{load})}$ (kg)
A	$[0, 1000]$	$(0, 0, 0)$	$(0.1, 0.1, 0.1)$	0	4.5	$(100, 0, 50)$
B	$[0, 364]$	$(0.25, 0.1, 0.1)$	$(0.51, 0.2, 0.2)$	0	4	$(72.8, 36.4, 0)$
C	$[300, 400]$	$(0.1, 0.1, 0.1)$	$(0.1, 0.1, 0.1)$	4	5.5	$(0, 0, 0)$
D	$[0, 364]$	$(0.25, 0.1, 0.1)$	$(0.51, 0.2, 0.2)$	2	6	$(72.8, 36.4, 0)$
E	$[300, 400]$	$(0.1, 0.1, 0.1)$	$(0.1, 0.1, 0.1)$	6	7.5	$(0, 0, 0)$

4.4 Example 3: multiple contaminant case

The third example is an adaptation of example 2 for a multiple contaminant environment as described in Table 4. The forbidden set of unit pairs for this example is defined as $\mathcal{I}^{\text{forbid}} = \{(\text{C}, \text{C}), (\text{E}, \text{E})\}$. The resultant network configurations and computation results are presented in Fig.s 6(a)-(d) and Table 5, respectively. It is worthy to note that although the operational constraints in terms of forbidden water recycles do not cause any penalty for the freshwater consumption and required storage capacity, the storage policy needs to be changed to meet a practical design.

5 Conclusions

Operations of water-using units in batch plants are almost time dependent. Nevertheless, such time dependence can be partially bypassed by equipping central storage facilities, to temporarily collect the reusable water from the earlier operations and then supply that water for the later operations. With a predefined production schedule, this paper has

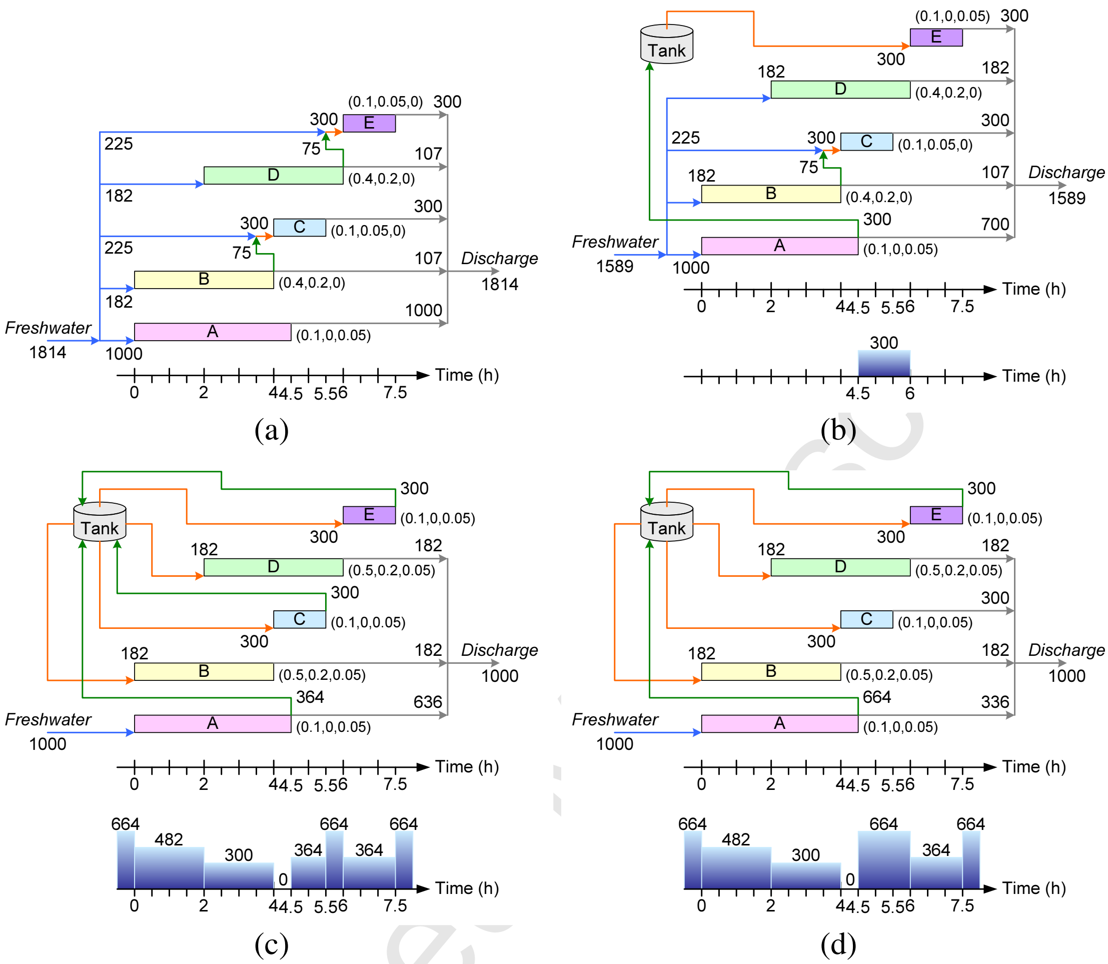

Figure 6: Resultant networks of example 3: (a) single operation without a storage tank, (b) single operation with one storage tank, (c) cyclic operation with one storage tank, and (d) cyclic operation with one storage tank after forbidding water recycle in units C and E.

Table 5: Computation results of example 3.

Operating mode	Single op.		Cyclic op.	
No. of storage tanks	0	1		
Forbidden recycle	No			Yes
Problem structure	**NLP**			**MINLP**
No. of constraints	1521	1681	1681	7285
Continuous variables	1201	1505	1505	1505
Discrete variables	–	–	–	1392
Freshwater (kg)	1814	1589	1000	1000
Storage cap. (kg)	0	300	664	664
CPU time (sec)	0.23	0.27	0.31	7.45

presented a mathematical formulation for synthesizing batch water-using networks with central storage tank(s). Superstructures incorporating all flow connections are constructed to assist the problem formulation. The minimum freshwater consumption is targeted, and both operating modes (single and cyclic operations) are included. The design problems is formulated as a nonlinear program (NLP) if there is no constraint on water reuse and recycle, or a mixed-integer nonlinear program (MINLP) when forbidding water reuse/recycle is taken into consideration. Representative examples adopted and adapted from literature are provided to demonstrate the good expectation of the proposed, superstructure-based NLP and MINLP formulations. The logical expressions developed in this work are applicable to the cases with single storage tank. More possibilities of flow connections should be comprehended when considering the cases with multiple storage tanks.

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Nomenclature

Indices and Sets	
$c \in \mathcal{C}$	$= \{1, ..., C\}$, contaminant species
$d \in \mathcal{D}$	$= \{1, ..., D\}$, discharge points
$i \in \mathcal{I}$	$= \{1, ..., I\}$, water-using units
$p \in \mathcal{P}$	$= \{1, ..., P\}$, time points
$p \in \mathcal{P}^*$	$= \{2, ..., P\}$, time points except the first one
$s \in \mathcal{S}$	$= \{1, ..., S\}$, storage tanks
$w \in \mathcal{W}$	$= \{1, ..., W\}$, water sources

Parameters	
$C^{(\text{in})}_{ic,\max}$	maximum inlet concentration of contaminant c of unit i
$C^{(\text{out})}_{ic,\max}$	maximum outlet concentration of contaminant c of unit i
C_{wc}	concentration of contaminant c in water source w
Δ_i	distance between time points of start/finish of the operation in unit i
$M^{(\text{load})}_{ic}$	mass load of contaminant c to be removed in unit i
Q^{L}_i	lower bound for the water requirement of unit i
Q^{U}_i	upper bound for the water requirement of unit i
Q^{L}_s	lower bound for the capacity of storage tank s
Q^{U}_s	upper bound for the capacity of storage tank s
$Q^{\text{L}}_{**'}$	lower bound for the connecting flow from $*$ to $*'$, $**' \in \{ii', is, si\}$
$Q^{\text{U}}_{**'}$	upper bound for the connecting flow from $*$ to $*'$, $**' \in \{ii', is, si\}$
$y^{(\text{st.})}_{ip}$	$\in \{0,1\}$, $= 1$ denotes unit i starting the operation at time point p
$y^{(\text{fin.})}_{ip}$	$\in \{0,1\}$, $= 1$ denotes unit i finishing the operation at time point p
$Z^{(\text{cyc.})}$	$\in \{0,1\}$, $= 1$ denotes cyclic operation

Binary variables	
$E_{spp'}$	$= 1$ means storage tank s was emptied during the time period p to p'
$X_{ii'p}$	$= 1$ means unit i' received the water from unit i at time point p
X_{isp}	$= 1$ means storage tank s received the water from unit i at time point p
X_{sip}	$= 1$ means unit i received the water from storage tank s at time point p
$Y^{(\text{occ.})}_{sp}$	$= 1$ means storage tank s keeps a finite storage at time point p
$Z_{ii'p}$	$= 1$ means existing flow from unit i to unit i' at time point p
Z_{isp}	$= 1$ means existing flow from unit i to storage tank s at time point p
Z_{sip}	$= 1$ means existing flow from storage tank s to unit i at time point p

Positive variables	
$C^{(\text{in})}_{icp}$	inlet concentration of contaminant c to unit i at time point p
$C^{(\text{out})}_{icp}$	outlet concentration of contaminant c from unit i at time point p
$C^{(\text{in})}_{scp}$	inlet concentration of contaminant c to storage tank s at time point p
$C^{(\text{out})}_{scp}$	outlet concentration of contaminant c from storage tank s at time point p
q_{idp}	water flow from unit i to discharge point d at time point p
$q_{ii'p}$	water flow from unit i to another unit i' at time point p
q_{isp}	water flow from unit i to storage tank s at time point p
q_{sip}	water flow from storage tank s to unit i at time point p
q_{wip}	water flow from water source w to unit i at time point p
$q^{(\text{in})}_{ip}$	inlet water flow to unit i at time point p
$q^{(\text{out})}_{ip}$	outlet water flow from unit i at time point p
$Q^{\max}_s$	maximum capacity of storage tank s
Q_{sp}	amount of remaining water in storage tank s at time point p
$q^{(\text{in})}_{sp}$	inlet water flow to storage tank s at time point p
$q^{(\text{out})}_{sp}$	outlet water flow of storage tank s at time point p

References

[1] Almato, M., Espuna, A., & Puigjaner, L. (1999). Optimization of water use in batch process industries. *Computers and Chemical Engineering*, *23*, 1427-1437.

[2] Bagajewicz, M., & Savelski, M. (2001). On the use of linear models for the design of water utilization systems in process plants with a single contaminant. *Transactions of the Institute of Chemical Engineers, Part A*, *79*, 600-610.

[3] Brooke, A., Kendrick, D., Meeraus, A., Raman, R., & Rosenthal, R. E. (2003). *GAMS: A User's Guide*. Redwood city: Scientific Press.

[4] Foo, D.C.Y., Manan, Z.A., & Tan, Y.L. (2005). Synthesis of maximum water recovery network for batch process systems. *Journal of Cleaner Production*, *13*(15), 1381-1394.

[5] Gunaratnam, M., Alva-Argaez, A., Kokossis, A., Kim, J.K., & Smith, R. (2005). Automated design of total water systems. *Industrial and Engineering Chemistry Research*, *44*(3), 588-599.

[6] Li, B.H., & Chang, C.T. (2006). A Mathematical Programming Model for Discontinuous Water-Reuse System. *Industrial and Engineering Chemistry Research*, *45*, 5027-5036.

[7] Majozi, T. (2005a). Wastewater minimisation using central reusable water storage in batch plants. *Computers and Chemical Engineering*, *29*, 1631-1646.

[8] Majozi, T. (2005b). An effective technique for wastewater minimisation in batch processes. *Journal of Cleaner Production*, *13*(15), 1374-1380.

[9] Majozi, T. (2006). Storage design for maximum wastewater reuse in multipurpose batch plants. *Industrial and Engineering Chemistry Research*, *45*, 5936-5943.

[10] Majozi, T., Brouckaert, C.J., & Buckley, C.A. (2006). A Graphical Technique for Wastewater Minimization in Batch Processes. *Journal of Environmental Management*, *78*(4), 317-329.

[11] Wang, Y.P., & Smith, R. (1994). Wastewater minimization. *Chemical Engineering Science*, *49*(7), 981-1006.

[12] Wang, Y.P., & Smith, R. (1995a). Wastewater minimization with flowrate constraints. *Transactions of the Institute of Chemical Engineers, Part A*, *73*, 889-904.

[13] Wang Y.P., & Smith R. (1995b). Time pinch analysis. *Transactions of the Institute of Chemical Engineers, Part A*, *73*, 905-914.

Captions of Figures and Tables

Figure 1 Superstructures for (a) water-using unit and (b) storage tank.

Figure 2 Gantt chart for the production schedule of example 1.

Figure 3 Resultant networks of example 1: (a) single operation without a storage tank, (b) single operation with one storage tank, and (c) cyclic operation with one storage tank.

Figure 4 Resultant networks of example 2: (a) single operation without a storage tank, (b) single operation with one storage tank, and (c) cyclic operation with one storage tank.

Figure 5 Revised networks after forbidding water reuse/recycle in units C and E: (a) single and (b) cyclic operation with one storage tank for example 1, and (c) cyclic operation with one storage tank for example 2.

Figure 6 Resultant networks of example 3: (a) single operation without a storage tank, (b) single operation with one storage tank, (c) cyclic operation with one storage tank, and (d) cyclic operation with one storage tank after forbidding water recycle in units C and E.

Table 1 Processing data for examples 1 and 2.

Table 2 Computation results of examples 1 and 2.

Table 3 Computation results of cases with forbidden reuse/recycle.

Table 4 Processing data for example 3.

Table 5 Computation results of example 3.