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Mathematical modelling of sustainable wastewater reuse networks considering CO_2 emissions

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Abstract−Water resource management poses a challenge in the process industry because a large amount of water must be used, even when prices increase. Companies struggle to minimize consumption by reusing wastewater, and the resulting water-reuse-network problem has been actively investigated. With the rising impact of global climate change, it is necessary to develop a sustainable methodology to reduce carbon dioxide emissions in the process industry. This paper proposes a mathematical model for sustainable water reuse networks that explicitly considers CO_2 emissions. To construct a sustainable network, emissions due to the construction and operation of the water network and additional water demand due to CO_2 capture facilities are incorporated. Actual case studies of steel manufacturing processes and eco-industrial parks are presented to illustrate the applicability of the model.

Keywords: Water Network, Carbon Dioxide, Carbon Capture and Storage (CCS), Sustainability, Optimization

INTRODUCTION

The depletion of water resources is an imminent issue as demand is continuously increasing worldwide, and water resources are becoming scarce [1]. Many methods have been considered to address the issue, such as seawater desalination and the reuse of wastewater. Reusing wastewater is cheaper and consumes less energy, but large-scale public water reuse has been relatively limited to arid countries such as the Middle East and Singapore (in Fig. 1 [2]). Some of the reasons are the potential health risks, low water prices, and a lack of public understanding.

There is considerable opportunity in the process industry to reuse wastewater. Water is a key resource for the industry because many unit processes consume a large amount of water, such as steam stripping, liquid-liquid extraction, and washing operations [3]. Wastewater can be used in these processes. However, it is a challenge to manage the multiple wastewater streams used in the processes to minimize the total amount of water. The water reuse network problem has attracted much attention [4-6].

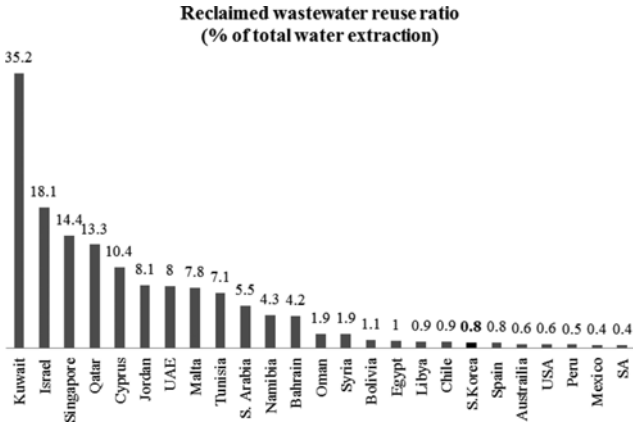

Fig. 1. Reclaimed water reuse percentages of total water usage [2].

Studies on wastewater networks can be categorized as graphical analyses and mathematical modeling. Graphical methods are generally based on pinch analysis, which was originally developed for heat transfer integration [7] and expanded to deal with multiple contaminants [8,9], improve targeting methods [10,11], and automate network generation [12-14]. Foo addressed various water pinch techniques based on works covering the introductory features and current research using the graphical method [15].

The mathematical modeling method considers all entities and their potential connections in the superstructure network to compute the best network configuration. Takama et al. [16] and Wang and Smith [8] were the first to introduce the superstructure concept for a wastewater reuse network by transforming it into a nonlinear programming (NLP) problem. The superstructure method was later extended by considering multiple variables [17], setting necessary optimality conditions [18], and dealing with nonlinear water quality properties [19]. The superstructure was later modified to represent inter-plant wastewater exchanges [20] and generalized wastewater reuse [21,22].

Various works have investigated the management of water demand from multiple plants in an eco-industrial park [23-26]. Existing wastewater networks have also been redesigned by retrofitting from the perspective of process design and synthesis [27,28]. The water network problem has also been integrated with other utility issues simultaneously, such as energy [29-31] and heat [32-34]. Jiménez-Gutiérrez et al. [35] investigated energy, mass, and water

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simultaneously.

Different computational methods have also been used. Most reuse network problems have been formulated into a mixed-integer NLP (MINLP) model. However, one major difficulty is the complexity due to the nonlinearity in the model. The solutions obtained with a general solver do not guarantee global optimality, or a long time is required for computation [21]. Several computation approaches have been thus proposed, including decomposing the MINLP into MILP or NLP [21,36,37], better initialization techniques [37], and metaheuristic approaches [38]. Quirante and Caballero [39] employed surrogate models to handle the network problem, and Ramos et al. [40] approached the problem in terms of goal programming.

Increased public interest in sustainable development has been driving economic activities to become more environmentally friendly by reducing greenhouse gas emissions. Sustainability is also an important issue in reusing industrial wastewater because a significant amount of CO_2 is generated during reclamation, as shown in Figs. 2 and 3. However, to the best of our knowledge, little research has been done on water reuse, energy, and CO_2 in this regard. Some studies focused on calculating CO_2 emissions based on energy usage in a single treatment unit or plant [43,44]. Additional water consumption due to separating or capturing CO_2 has attracted little attention except for power generation facilities. Some works on thermoelectric plants addressed the impacts of carbon capture on water demand [45]. Zhai et al. [46] analyzed the water usage of MEA absorption and its impact on the water consumption of pulverized coal power plants. Other studies examined electricity usage in residential areas [47].

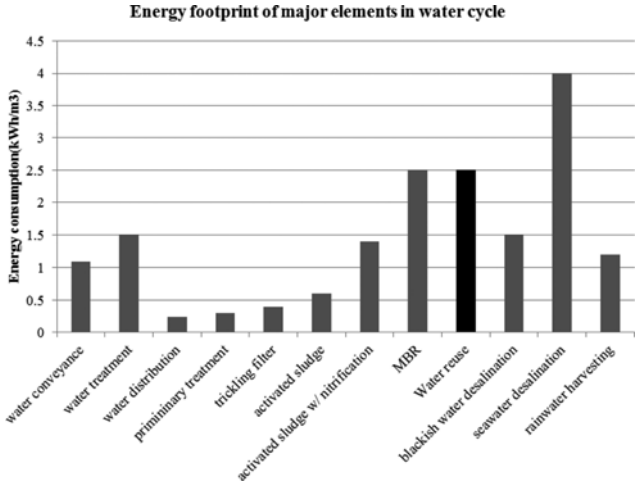

Fig. 2. Typical energy footprint of major elements and processes in water cycling [41].

The increased use of electricity from reusing wastewater causes additional CO_2 emissions. Companies are beginning to make greater efforts to reduce CO_2, such as through carbon capture and storage (CCS) facilities. However, these facilities require water and increase total consumption. This paper addresses CO_2 emissions from water handling and the additional water consumption due to CO_2 reduction in the water reuse network in a decision-making framework. The framework is used to make computations for sustainable water reuse networks. The formulation of the general wastewater network superstructure is first presented, and then the superstructure is modified to reflect the sustainability feature. Case studies are presented to illustrate the applicability of the models.

FORMULATION OF A GENERAL WASTEWATER NETWORK SUPERSTRUCTURE

A superstructure is constructed in consideration of all entities in the water reuse network and their possible connections in the mathematical formulation. The connections include splits and merges. Many researchers have addressed the general superstruc-

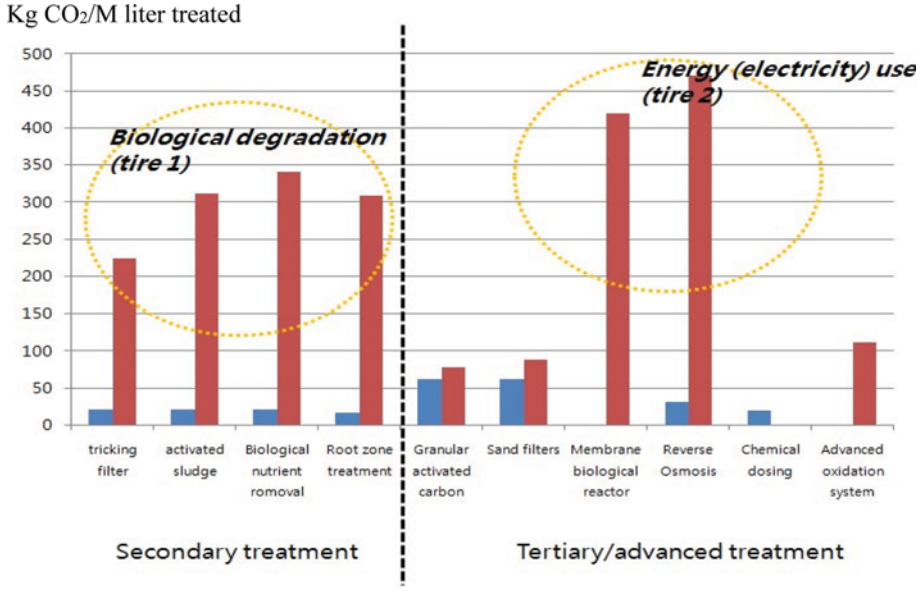

Fig. 3. CO_2 emissions from a range of wastewater treatment options [42].

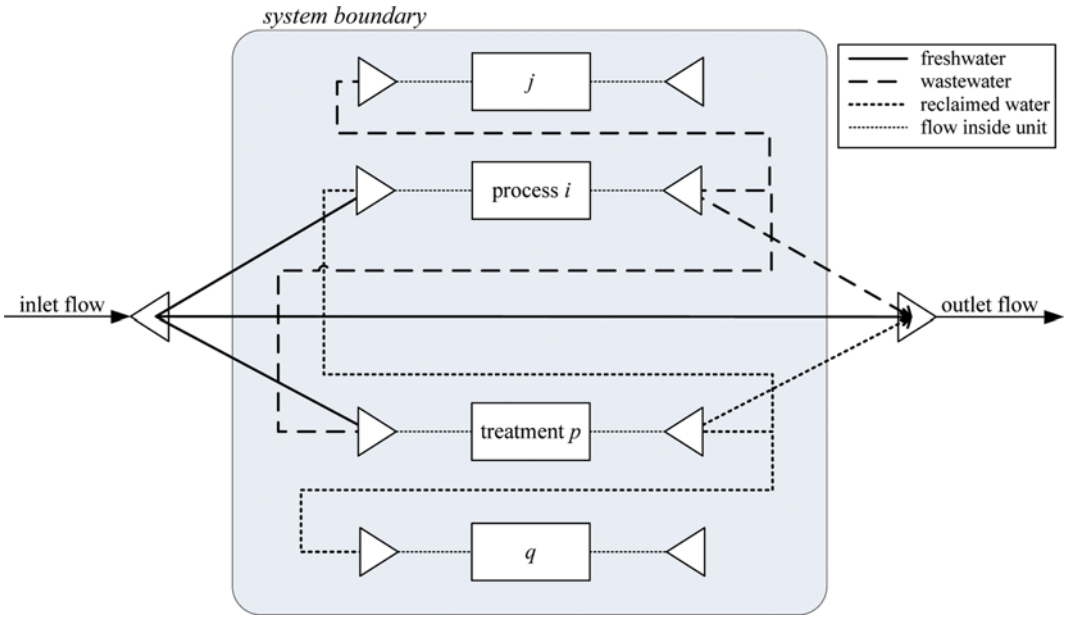

Fig. 4. General superstructure of a water treatment process.

ture of wastewater reuse in the process industry, including Grossmann [22] and El-Halwagi [20]. Most models are based on the common concepts of "splitters" and "mergers" in handling the flows, although they show significant variations in several points, including the formulation of inter-plant water reuse.

Fig. 4 shows the general water flow superstructure in the case of a single freshwater source and a wastewater discharge sink. The case of multiple sources and sinks can be extended from this case.

As shown in Fig. 4, a system consists of two types of units. A "process" unit denotes a water-consuming facility that is either a manufacturing or non-manufacturing facility. It is regulated in terms of the inlet flow rate or quality. A "treatment" unit represents a water treatment facility. The inlet and outlet conditions of both units are constrained.

1. Process Unit Balance

The water demand of process unit i can be met by three types of water sources, as illustrated in Fig. 5. A process water inlet (pwi_i) can be the sum of the following three terms: freshwater (fw_i), untreated wastewater ($bw_{j,i}$), and reclaimed water ($rw_{p,i}$).

$$pwi_i = fw_i + \sum_j bw_{j,i} + \sum_p rw_{p,i} \tag{1}$$

For most manufacturing processes, treated (or recycled/reclaimed) water is used. It is because the process operator in charge of the process can manage only a limited number of pollutant species. Outsourced wastewater may contain various other pollutant species beyond the manageable level. The presence of such unnoticed pollutants in the outsourced treated water may seriously affect the process condition. On the other hand, it is also true that fresh water is used as well to dilute the concentration in the wastewater, and some pre-tested treated water can be used to increase the total amount of wastewater. In practice, the key pollutant species are carefully selected in the actual wastewater management. The resulting process constraints are added and revised by gradually increasing the pollutant species.

The sum of the mass or contaminant load in the inlet water flow into the process unit i should not violate the limit mass load.

$$Cpwi_{i,x}^{low} pwi_i \le Cfw_{i,x} fw_i + \Sigma_j Cbw_{j,i,x} bw_{j,i} + \Sigma_p Crw_{p,i,x} rw_{p,i} \le Cpwi_{i,x}^{high} pwi_i \tag{2}$$

The wastewater flow from the process water outlet (pwo_i) consists of three flows:

$$pwo_i = \Sigma_j bw_{i,j} + \Sigma_p ww_{i,p} + dw_i \tag{3}$$

where index j denotes untreated wastewater units and p denotes wastewater units.

The water qualities of the divided flows are assumed to be identical.

$$Cpwo_{i,x} = Cbw_{i,j,x} = Cww_{i,p,x} = Cdw_{i,x} \quad \forall i, x, j, p \tag{4}$$

2. Treatment Unit Balance

As shown in Fig. 6, the inlet water flow twi_p and mass load of treatment unit p is the sum of the wastewater to be treated in the process units and the water from the freshwater source and treatment units.

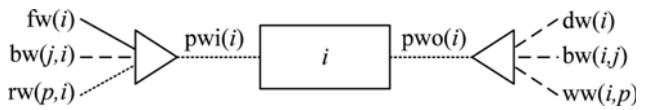

Fig. 5. Process unit balance.

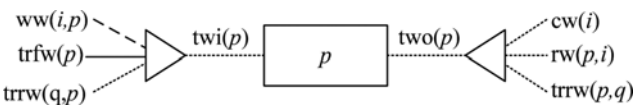

Fig. 6. Balance in a treatment unit.

$$\mathrm{twi}_p = \Sigma_i \mathrm{ww}_{i,p} + \mathrm{trfw}_p + \Sigma_q \mathrm{trrw}_{q,p} \quad (5)$$

$$\mathrm{Ctwi}_{p,x}\mathrm{twi}_p = \Sigma_i \mathrm{Cww}_{i,p,w}\mathrm{ww}_{i,p} + \mathrm{Ctrfw}_p\mathrm{trfw}_p + \Sigma_q \mathrm{Ctrrw}_{p,q,x}\mathrm{trrw}_{p,q} \quad (6)$$

Reclaimed water from the treatment unit p is either discharged to the surroundings as cw_p, mixed into other treatment units as $trrw_{p,q}$, or reused in process units as $rw_{p,i}$.

The treatment water outlet is the sum of the three terms:

$$\mathrm{two}_p = \mathrm{cw}_p + \Sigma_i \mathrm{rw}_{p,i} + \Sigma_q \mathrm{trrw}_{p,q} \quad (7)$$

The water qualities of the flows are identical, as in a process unit.

$$\mathrm{Ctwo}_{p,x} = \mathrm{Ccw}_{p,x} = \mathrm{Crw}_{p,i,x} = \mathrm{Ctrrw}_{p,q,x} \quad (8)$$

The operation in treatment facility can be constructed according to the relationship between its inlet and outlet flows. In terms of quantity, partial water loss is a common phenomenon in wastewater treatment and is expressed in Eq. (9):

$$\mathrm{two}_p = \mathrm{trloss}_p \mathrm{twi}_p \quad (9)$$

The concentration regenerated from a treatment center is proportional to the inlet quality. As contaminated wastewater comes into the facility, the quality of discharged water also deteriorates. However, some treatment facilities emit reclaimed water with fixed qualities, regardless of the source water. This characteristic is specified based on the selected treatment technology. Moreover, a treatment facility may have mixed characteristics, which is addressed in Eq. (10). Two parameters are entered in the equation based on the treatment technology selection. The coefficient $ptr_{a,x}$ represents the proportional treatment ability of the technology, while the constant $ptr_{b,x}$ means a fixed outlet concentration of the second type of the facility mentioned, and $ptr_{a,x}$ should be set to zero(0) in this case.

$$\mathrm{Ctwo}_{p,x} = \mathrm{ptr}_{a,x}\mathrm{Ctwi}_{p,x} + \mathrm{ptr}_{b,x} \quad (10)$$

3. Total System Balance

The total amount of freshwater needed in the system (tfw) is the sum of the freshwater supplied to the process units, the dilution water for the treatment facilities, and the water directly discharged to the surroundings (dfw), as shown in Fig. 7. The water quality remains the same.

$$\mathrm{tfw} = \Sigma_i \mathrm{fw}_i + \mathrm{dfw} + \Sigma_p \mathrm{trfw}_p \quad (11)$$

$$\mathrm{Crfw}_x = \mathrm{Cfw}_{i,x} = \mathrm{Cdfw}_x = \mathrm{Ctfw}_p \quad \forall \mathrm{i, x, p} \quad (12)$$

The total amount of wastewater discharged from the entire system to the surroundings is the sum of the wastewater discharged directly from the process units (dw_i), treated water from the treatment units (cw_p), and dilution water from the freshwater source. Generally, the final discharge regulations are assigned to a factory or industrial complex. Therefore, Eqs. (13)-(15) are introduced to limit the contamination level of the outlet discharge.

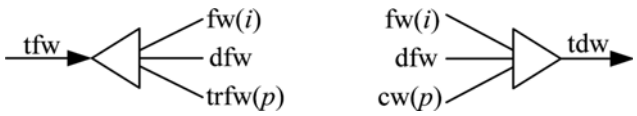

Fig. 7. Freshwater source splitter and wastewater discharge merger.

$$\mathrm{tdw} = \Sigma_i \mathrm{dw}_i + \mathrm{dfw} + \Sigma_p \mathrm{cw}_p \quad (13)$$

$$\mathrm{Ctdw}_x \cdot \mathrm{tdw} = \Sigma_i \mathrm{Cdw}_{i,x}\mathrm{dw}_i + \mathrm{Cdfw}_x\mathrm{dfw} + \Sigma_p \mathrm{Ccw}_{p,x}\mathrm{cw}_p \quad (14)$$

$$\mathrm{Cdlimit}_x^{low} \le \mathrm{Ctdw}_x \le \mathrm{Cdlimit}_x^{high} \quad (15)$$

4. Objective Function

The objective is to minimize the total cost of the wastewater network. The corresponding objective function in the network model involves the following cost factors:

- Freshwater price: Freshwater from an external source should be purchased at a certain price.
- Wastewater discharge cost: When wastewater is discharged to the surroundings, it should satisfy the quality regulations. An additional tax is levied for the discharged water in various countries, including South Korea. The levy is normally proportional to the discharged quantity.
- Reclaimed water price: Reclaimed water is substituted for freshwater and there are also charges for its use. The price of reclaimed water is normally lower than that of freshwater, mainly because of governmental subsidies. Additional piping and pumping expenses due to water reuse were also included in the reclaimed water expense.
- Wastewater treatment cost (capital/operational): When a wastewater treatment facility is introduced to provide reclaimed water to a system, its construction cost should be covered. The inclusion of the facility's capital cost in the total cost is optional because it is sometimes paid by governments or other external groups, which should be specified before computation. The operation cost is normally proportional to the wastewater flow rate into the facility and should be charged as well. Generally, the operation cost is paid by the actual wastewater dischargers or reclaimed water users through billing or taxation.

Based on these considerations, Eq. (16) was formulated as an objective function for the overall cost.

$$\begin{aligned}\mathrm{tcost} = {} & \mathrm{tfw}\cdot\mathrm{price}_{fw} + \mathrm{tdw}\cdot\mathrm{price}_{dw} \\ & + (\Sigma_p\Sigma_i \mathrm{rw}_{p,i} + \Sigma_m\Sigma_i \mathrm{rwccs}_{m,i})\cdot\mathrm{price}_{rw} \\ & + \mathrm{trcapital}_p \frac{\mathrm{twi}_p}{\mathrm{twi}_p + \varepsilon} + \mathrm{troper}_p \cdot \mathrm{twi}_p\end{aligned} \quad (16)$$

Parameter ε is a relatively small number and was included in the capital cost term to avoid using binary variables. The overall optimization can be formulated by aggregating the constraints and objective function into the following MILP problem:

Min (16)
s.t. (1)-(15)

THE INTEGRATION OF WATER REUSE NETWORK AND CCS

CO_2 is generated from wastewater treatment because it involves biodegradation processes that consume a significant amount of energy [48]. It is necessary to deal with the CO_2 emissions in carbon capture facilities under strengthened CO_2 regulations. The water flow should be increased to meet the additional water demand

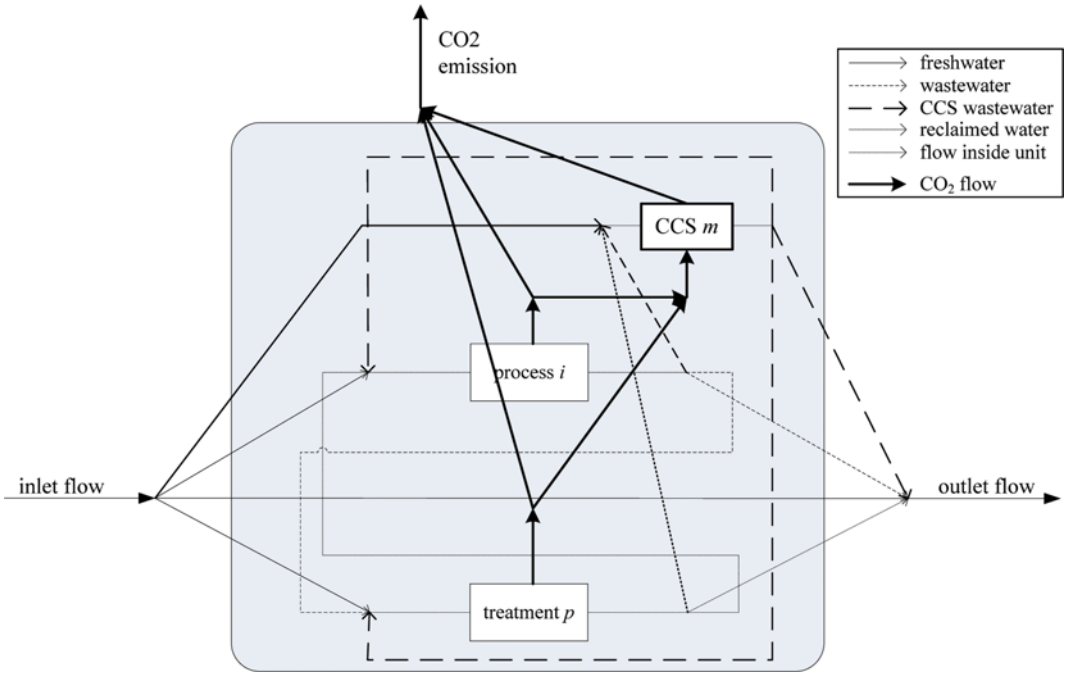

Fig. 8. General water network superstructure including CO_2 flow and carbon capture facility.

from these new capture facilities because they also consume a significant amount of water. The network model in the previous section should be revised to reflect the presence of CO_2 emissions and capture facilities. Two modified models are thus proposed.

1. Modified Model I: Introduction of Direct CO_2 Emission and Carbon Capture Facilities

In modified model I, the capture facilities are assumed to be "process" units. Each unit accepts freshwater and regenerated water, like other process units in the system. Fig. 8 illustrates this modified water flow after introducing CO_2 emission and carbon capture facilities to the network.

The CO_2 flow and capture activity in the water reuse network are represented by Eqs. (17), (18), and (19). A new index m is used to handle the capture facilities because they can be introduced for any single unit process or group of processes. As shown in Fig. 9, the indices of the directly recycled water bw are extended from (i, j) to ([i, m], [j, n]) because a direct recycle link can be made between process units and capture units.

$$\mathrm{pCO2}_m = \mathrm{p0CO2}_m - \mathrm{pccsCO2}_m \cdot \mathrm{pcap}_m \quad \forall \mathrm{m} \tag{17}$$

The capacity should remain within the upper bound:

$$\mathrm{pccsCO2}_m \le \mathrm{ccscapa}_m \quad \forall \mathrm{m} \tag{18}$$

The total amount of CO_2 is the sum of the individual parts:

$$\mathrm{tCO2} = \Sigma_m \mathrm{CO2}_m \tag{19}$$

The unit process index i is extended to [i, m] as in the CO_2 flow. The cost objective function is also modified by adding carbon capture costs.

$$\begin{aligned}\mathrm{tcost} = {} & \mathrm{tfw}\cdot\mathrm{price}_{fw} + \mathrm{tdw}\cdot\mathrm{price}_{dw} \\ & + \Sigma_p \Sigma_{[i,m]} \mathrm{rw}_{p,[i,m]} \cdot \mathrm{price}_{rw} \\ & + \mathrm{trcapital}_p \cdot \frac{\mathrm{twi}_p}{\mathrm{twi}_p + \varepsilon} + \mathrm{twi}_p \cdot \mathrm{troper}_p \\ & + \mathrm{capcapital}_m \cdot \frac{\mathrm{pccsCO2}_m}{\mathrm{pccsCO2}_m + \varepsilon} \\ & + \mathrm{pccsCO2}_m \cdot \mathrm{capoper}_m\end{aligned} \tag{20}$$

where the price term denotes the unit price coefficient of each variable, and the $\mathrm{trcapital}_p$, $\mathrm{capcapital}_m$, and $\mathrm{capoper}_m$ terms represent the capital cost and operation cost variables of a water treatment and CCS facility. The overall optimization can be formulated as a summation of the constraints and objective function:

Min (20)
s.t. (1)-(15)
s.t. (17), (18), (19)

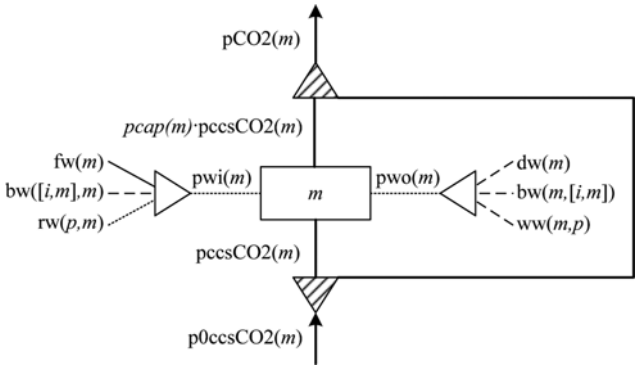

Fig. 9. Water and CO_2 balance of a capture facility m.

2. Modified Model II: Indirect CO_2 Emission and Emission from the Construction Period

For the accurate evaluation of CO_2 emissions, it is appropriate

to categorize the emission sources. For example, the emission from coke or the combustion of other fuels has been classified as *direct emissions* or *Scope 1 emissions* according to the World Resource Institute's CO_2 protocol. Other types of emissions that are not directly generated from processes include *Scope 2 emissions*, such as externally purchased electricity [49].

Modified model I considers only direct CO_2 emissions and does not consider the additional electricity use due to the increased wastewater treatment and pumping. A significant amount of CO_2 is generated in the construction of treatment facilities [52]. *Modified model II* therefore incorporates indirect emissions and those from the construction stage. The two major changes are the following:

- A time index t is introduced to interpret the construction period. Unless facilities or pipes were built before the period of consideration, they should be constructed at a certain point.

- Binary variables $link_t$ is introduced to denote the construction status of the facilities and pipes. The disassembly of facilities was not considered. Once a facility or pipe is installed, it is not required to reconstruct another one when water flow resumes after temporarily stopping.

Although there was no significant change in the balance equations other than the inclusion of index t in all variables, the equations representing the pipes and facilities were added to the model.

2-1. Existence of Pipes and Facilities

Eqs. (21) and (22) are mathematical formulations of the pipe construction to each linkage:

$$\begin{aligned} &link_t \geq link_{t-1},\ d, e \in [i, m];\ link_t \in [0, 1];\\ &link_t \in [Ifw_{d,t}, Idw_{d,t}, Ibw_{d,e,t}, Iww_{d,p,t}, Irw_{p,d,t},\\ &\quad Itrfw_{p,t}, Itrrw_{p,q,t}, Icw_{p,t}, Idfw_t] \end{aligned} \tag{21}$$

$$link_t \geq \frac{flow_t}{flow_t + \varepsilon} \tag{22}$$

$$flow_t \in [fw_{d,t}, dw_{d,t}, bw_{d,e,t}, ww_{d,p,t}, rw_{d,p,t}, trfw_{p,t}, trrw_{p,q,t}, cw_{p,t}, dfw_t]$$

As with piping, binary variables were assigned to wastewater treatment facilities and carbon capture facilities to represent their beginning of service.

$$Ifacility_{f,t} \geq Ifacility_{f,x-1},\ \ f \in [p, m>1] \tag{23}$$

$$Ifacility_{m,t} \geq \frac{pwi_m}{pwi_m + \varepsilon} \tag{24}$$

$$Ifacility_{p,t} \geq \frac{twi_p}{twi_p + \varepsilon} \tag{25}$$

2-2. CO_2 Emission and Cost Objective Function

The total cost and CO_2 balance equations were modified by including the capital cost and CO_2 emission at the point of construction. The emission from wastewater treatment In the CO_2 balance is also introduced and was not considered in modified model I. Eq. (28) represents the total CO_2 emission from the system in time period t, whereas (29) represents the total cost of the system in the time period.

$$pCO2_{f,x} = P0CO2_{f,t} - pccsCO2_{f,t} \cdot pcap_{f,t} \tag{26}$$

$$pccsCO2_{f,t} \leq ccscapa_{f,t} \cdot Ifacility_{f,t} \tag{27}$$

$$\begin{aligned} tCO2_t = {} & \Sigma_f pCO2_{f,t} + (Ifacility_{f,t} - Ifacility_{f,t-1}) \cdot \\ & constructCO2_f + (link_t - link_{t-1}) \cdot flow_t\ pipeCO2 \end{aligned} \tag{28}$$

$$\begin{aligned} tcost_t = {} & tfw_t \cdot price_{fw} + tdw_t \cdot price_{dw} + \Sigma_p \Sigma_d rw_{p,d,t} \cdot price_{rw}\\ & + (Ifacility_{p,t} - Ifacility_{p,t-1}) \cdot trcapital_p\\ & + twl_{p,t} \cdot troper_p + (Ifacility_{f,t} - Ifacility_{f,t-1}) \cdot cacapital_m\\ & + pccsCO2_{m,t} \cdot capoper_m + (link_t - link_{t-1}) \cdot pipecost \quad \forall t > 1 \end{aligned} \tag{29}$$

2-3. Introduction of Carbon Tax and Emission Certificates

Excessive CO_2 emissions are sometimes allowed upon paying an additional charge, which is called a carbon tax. When the amount of CO_2 emitted by a corporation or nation is below the pre-arranged limit, a marginal amount of emissions can be transferred to others, which requires extra emission allowances in return for reduction emission certificates. When the concept of carbon tax and emission certificates is introduced to the system, the total cost function can be modified with additional carbon cost terms.

The limitations of annual CO_2 emissions were assumed to be proportional to the system's initial emission based on the current strategy of the South Korean government. Eq. (30) shows the CO_2 emission regulation in a time period t, and (31) shows the revised cost objective function with a carbon tax and emission certificates. Eq. (30) is not mandatory for every time period. The emission constraints can be applied to selected periods or even to the final period only.

$$CO2limit_t = tCO2_t - taxCO2_t + cerCO2_t \tag{30}$$

$$\begin{aligned} tcost_t = {} & tfw_t \cdot price_{f,w} + tdw_t \cdot price_{d,w} + \Sigma_p \Sigma_d rw_{p,d,t} \cdot price_{r,w}\\ & + (Ifacility_{p,t} - Ifacility_{p,t-1}) \cdot trcapital_p\\ & + twi_{p,t} \cdot troper_p + (Ifacility_{f,t} - Ifacility_{f,t-1}) \cdot cacapital_m\\ & + pccsCO2_{m,t} \cdot capoper_m + (link_t - link_{t-1}) \cdot pipecost\\ & - taxCO2_t \cdot tax_t + cerCO2_t \cdot CER_t \end{aligned} \tag{31}$$

The modified model II can be formulated into the following mixed integer programming (MILP) problem:

Min (31)
s.t. (1)-(15)
(21)-(30)

CASE STUDY

Two practical case studies are presented to illustrate the applicability of the proposed models. First, the water usage in an integrated iron and steel mill is investigated as a case of internal wastewater reuse. Next, a wastewater reuse network in an industrial park is examined as an inter-plant case study. The two cases differ in the following ways:

· Number of CO_2 emission constraints: While the inner plant case is subject to a single CO_2 emission constraint, the plants in the inter-plant case have their own CO_2 limits, which require multiple constraints in the system.

· Variety in wastewater quality: The internal plant case shows more variety in wastewater quality than the inter-plant case, which allows for more changes to the system. This is mainly due to the effluent limit assigned to each facility in the case of inter-plant wastewater reuse.

Table 1. Water and wastewater characteristics of the steel mill case [50]

	Process water					Effluent				
	Item	Quantity (m^3/day)	Quality limit			Item	Quantity (m^3/day)	Quality		
			COD	TSS	pH			COD	TSS	pH
Coke oven	Quenching	3384	-	10	6-9	Quenching	960	42	21	8.1
	Gas cleaning	3864	10	-	6-9	Gas cleaning	2040	45	9.2	7.4
	Circulating cooling	1512	75	100	-	Circulating cooling	744	18.6	10.9	7.9
Sinter plant	Gas cleaning	1440	10	-	6-9	Gas cleaning	1200	45	18	8.5
	Other	1440	5	5	8-10	Other	1200	8	9	7.7
Pelletizing plant	Gas cleaning	2040	10	-	6-9	Gas cleaning	1128	47	3	6.8
	Other	1248	5	5	8-10	Other	0	-	-	-
Blast furnace	Circulating cooling	5160	75	100	-	Circulating cooling	0	-	-	-
	Gas cleaning	0	-	-	-	Gas cleaning	3480	10.3	11.5	7.7
	Granulation	6792	10	-	6-9	Granulation				
BOF	Gas cleaning	6360	10	-	6-9	Gas cleaning	4132	2.7	22	10.2
	Other	1632	5	5	8-10	Other	2324	8	8.5	7.2
Casting	Circulating cooling	5688	75	100	-	Circulating cooling	1224	45	15	8.7
Hot rolling	Circulation cooling	4560	75	100	-	Circulation cooling	2136	28	14	8.4
	One-through cooling	13008	75	500	5.0-8.3	One-through cooling	13008	19.3	12.3	7.7
Cold rolling	Circulation cooling	792	75	100	-	Circulation cooling	200	28	14	8.4
	Other	6192	10	-	6-9	Other	2008	38	57	7.6
Utilities	General	1314	3	5	6.5-7.5	General	0	-	-	-
	General	12600	10	-	6-9	General	1474	49	10	7.7
Raw material handling	General	1824	5	5	8-10	General	1824	17	48	7.8
	General	1032	10	-	6-9	General	0	-	-	-
CWD cooling	Cooling	2000	75	100	-	Cooling	2000	14.7	6.4	7.3

Table 2. Treatment options in the internal plant case

	Treatment efficiency/effluent quality				Capital cost (KRW)	Operation cost (KRW)	CO_2 emission ($kgCO_2/t\ H_2O$)	
	COD	TSS	pH	Cl-			Cap.	Oper.
GAC	97% (max.5)	1	7.2	-	80	60	80	78
MF	90%	0.3	8.0	250	80	80	200	22.4
RO	95%	0.1	7.0	150	40	120	40	370

The models were formulated, and their solutions were computed using the DICOPT solver in GAMS 23.6.3. An Intel 2.67 GHz Windows machine with 4.00 GB of RAM was used for computations.

1. Case Study I: Internal Plant Case

A steel mill emits considerable amounts of CO_2, mainly in the form of process off-gas, such as BFG (blast furnace gas, CO_2%= 20-25%), COG (coke oven gas, CO_2%=3-5%), LDG (Linz Donawitz Gas, CO_2%=15-20%), and boiler gases [50]. The original water flow network was simplified by excluding the seawater once-through cooling, and the existing reuse flow processes that discharge multiple water flows with different qualities were considered to be separate, such as the granulation process in the blast furnace. All processes are therefore represented as single input single output (SISO) models. The system consists of 25 process blocks. COD, TSS, and pH were considered as water quality parameters. Because pH is not a linear parameter, it should be modified before being using it as a parameter, which was done using El-Halwagi's property mixing method [20]. Table 1 summarizes the process water flow rates and the qualities of the steel mill.

Microfiltration (MF) and a granular activated carbon filter (GAC) were chosen as specific wastewater treatment technologies. Table 2 summarizes their data, including the treatment efficiency, capital and operation cost, and CO_2 emission factor. The capital costs of the treatment facilities were assumed to be charged to the steel mill and included in the objective function.

Although there were other CO_2 emission flows in the steel mill, it was assumed that the CO_2 capture facility constructions were allowed in only the blast furnace, coke oven, BOF, and utility units because other CO_2 emissions cannot be captured easily before discharging into the surroundings. Table 3 lists the off-gas streams considered in the case study. A range of CO_2 capture technologies are currently available, but this study assumes that MEA absorption is the only available option because it is the most widely used

Table 3. Off-gas characteristics [50]

	BFG	COG	LDG	Utility off-gas
Production volume (Nm^3/hr)	141,600	92,000	28,100	631,180
CO_2 concentration (vol %)	20	10	15	11.2
CO_2 load (kg/hr)	55,600	26,000	1,100	138,860

Table 4. MEA system parameters and other information [14]

Parameter		Value
MEA plant	CO_2 removal efficiency	90%
	Makeup water consumption	800 kg/Nm^3 flue gas
	Cooling water consumption	91.2 kg/kgCO_2
	Heat requirement for solvent regeneration	3517 kJ/kgCO_2
	Max. capacity	100,000 tonCO_2/yr/plant
	Capital cost	30,000 Korean won/tCO_2
	Operation cost	15,000 Korean won/tCO_2
Natural gas	Natural gas heat value	52,620 kJ/kg NG
	Natural gas utilization efficiency	75%
	Natural gas CO_2 emission	2.8 kgCO_2/kg NG
Cost information	Freshwater	620 Korean won/ton
	Wastewater discharge	45 Korean won/ton
	Reclaimed water	360 Korean won/ton
	Natural gas	290 Korean won/kg NG
	Carbon tax (tax_t)	15,000 Korean won/tCO_2
	Emission certificate (CER_t)	12,000 Korean won/tCO_2

and has the highest capacity [51].

When an MEA absorption plant is introduced to the system, additional energy must be consumed to regenerate the MEA solution [14]. The required energy was assumed to be generated by a CHP gas turbine using natural gas. The natural gas cost was thus included in the operation cost of the facility. Additional CO_2 emission from the natural gas consumption was also considered. Table 4 lists the performance and utility parameters of the MEA plant considered in the case study, as well as other parameters such as cost information.

Fig. 10 shows the amount of freshwater used and the wastewater discharged when implementing the proposed models. As expected, the introduction of carbon capture facilities increases water demand by more than 10%, which can partially be satisfied by the wastewater generated within the steel mill. Wastewater reuse covered 28.1% of the additional demand in the model I results. However, it covered only 12.1% in the model II results.

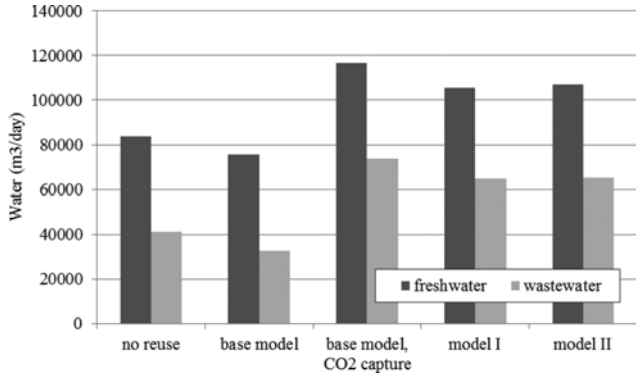

Fig. 10. Amount of freshwater usage/wastewater discharge for each model.

When indirect emission was considered, the amount of wastewater reuse decreased to approximately 87% compared to the case that did not consider indirect emission. This trend did not change even when carbon tax and certificates were introduced, which suggests that the water expenses were relatively small compared to the carbon-related prices. Figs. 11 and 12 show different wastewater reuse network structures based on the different models.

Because the formulated model includes the time variable t, the changes in wastewater reuse due to strengthening CO_2 regulations were also analyzed. As the limits on CO_2 emission are strengthened, the required capture capacity and water demand also increase. To deal with the increased water requirement, the amount of reuse must also increase, as shown in Fig. 13. Notably, the amount of capture required exceeded the capacity of a single capture plant in year 10, and a new plant had to be constructed. While the total cost and water requirement increased because of the new facility, water reuse kept increasing at almost the same ratio as in prior years.

2. Case Study II: Inter-plant Case

The eco-industrial park considered in this case study is located in an eco-industrial park and consists of 15 plants that discharge

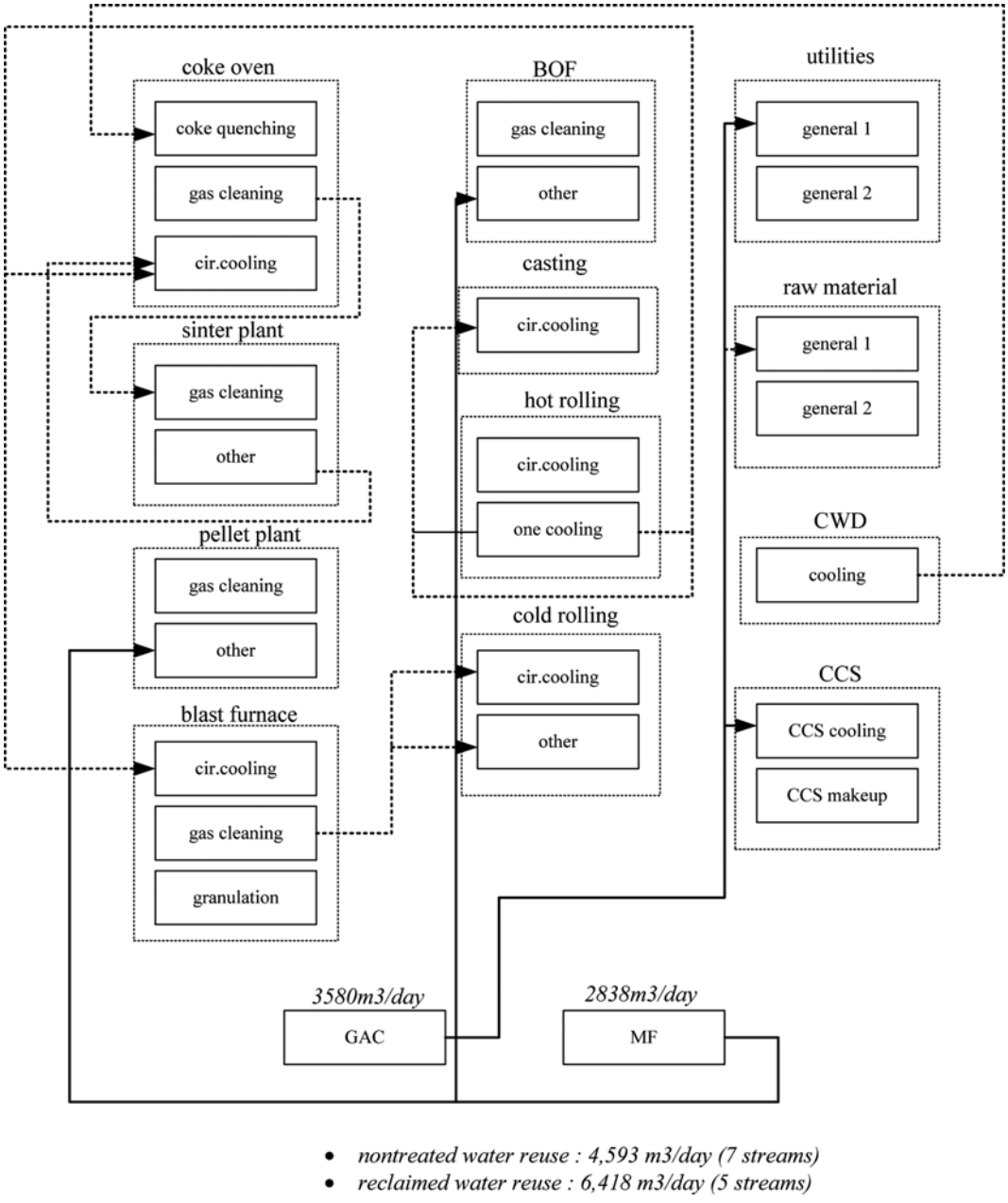

Fig. 11. Wastewater reuse network developed according to modified model I.

wastewater that is highly contaminated with chemicals. These plants include general, cement, chemical, and textile plants. Three water quality parameters were selected: chemical oxygen demand (COD), Cl^-, and total suspended solids (TSS). The wastewater discharging qualities are kept confidential in some plants and could not be obtained. Therefore, standard wastewater qualities were assigned to the plants in each category if they were not specified. Table 5 lists the water and wastewater characteristics as well as the CO_2 emission data for these plants.

Reverse osmosis (RO) and microfiltration were selected as the treatment technology options. In this case, the capital costs of the treatment facilities were assumed to be paid by the government, and their capital cost terms in the objective function were excluded. Information on the treatment options is summarized in Table 2.

Unlike in the internal plant case, carbon capture facilities were assumed to be available in every process unit. MEA absorption was introduced in this case, and the data related to the facilities can be found in Table 4. Additional energy consumption and CO_2 emissions from carbon capture facilities were not considered.

Fig. 14 shows the resulting amount of freshwater use and wastewater discharge. The results are similar to the previous case. In this case, the introduction of carbon capture facilities generated additional water demand (>45%). However, the demand was partially satisfied by the water reclaimed from the MF, and the incremental freshwater demand decreased to 21.4% and 29.4% in models I and II, respectively.

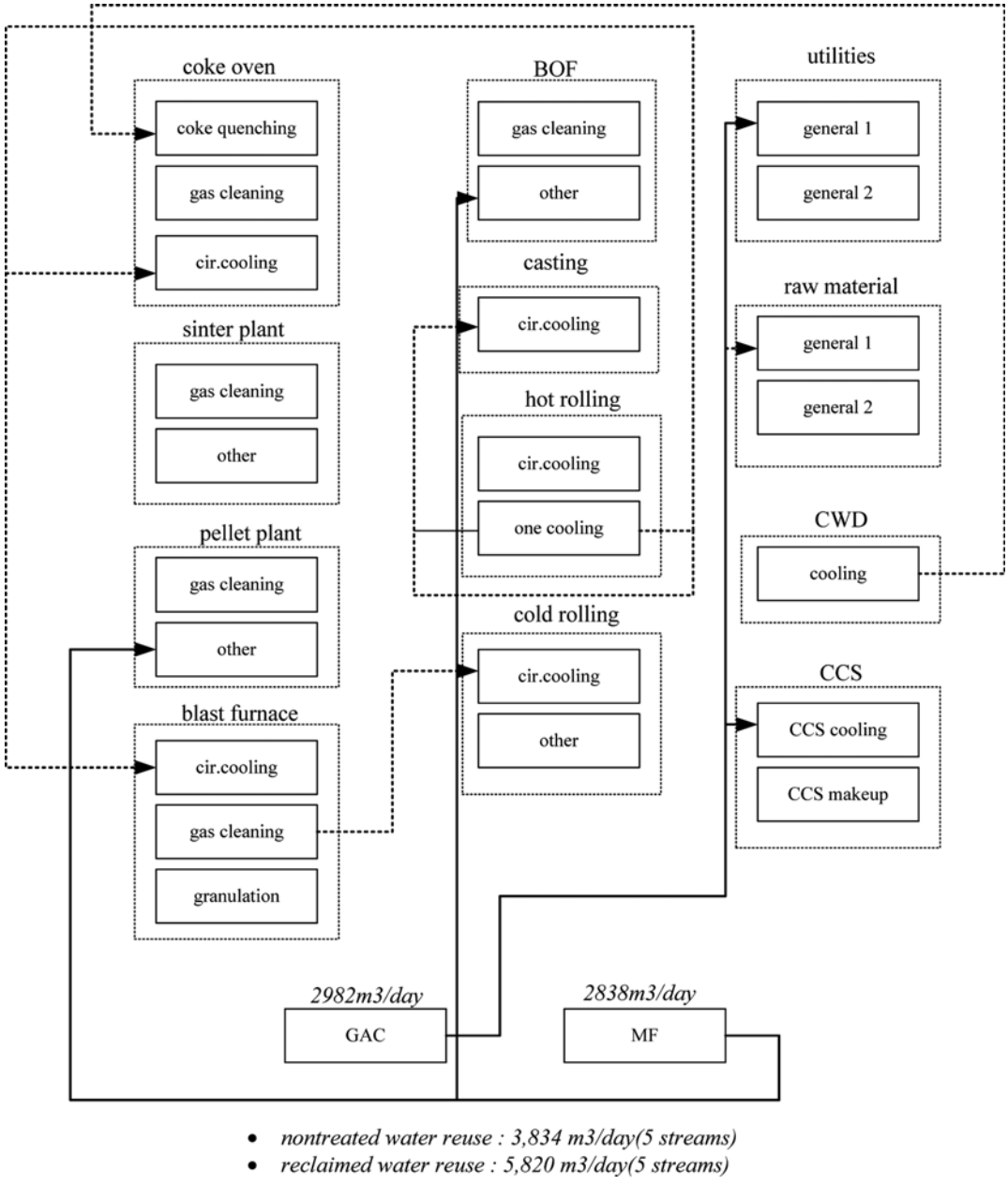

Fig. 12. Wastewater reuse network developed according to modified model II.

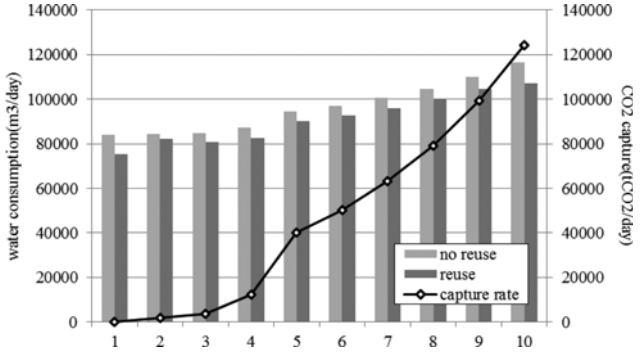

Fig. 13. CO_2 emission and freshwater consumption under the scheduled emission limits.

One of the major differences in this case compared to the previous one is its higher dependence on reclamation facilities. In the internal plant case, approximately 40% of the reused water was used with regeneration, and the rate did not change much when applying model II. In this case, however, the change in untreated water use was significant, as shown in Figs. 15 and 16. The lower quality and variation of the wastewater can explain this situation. The inlet quality demands could not be met easily with untreated water only, so mixing with freshwater or reclaimed water became essential when reusing the untreated wastewater. Therefore, the amount of untreated water decreased drastically when harder limits on reuse were applied, while the reclaimed water remained constant because the higher quality still gave an advantage over indirect

Table 5. Water and wastewater characteristics of an eco-industrial park case

	Plant type	Water demand (ton/day)	Wastewater discharge (ton/day)	CO_2 emission (ton/day)	Inlet quality requirement			Wastewater quality		
					COD	TSS	Cl-	COD	TSS	Cl-
1	Cement	8021	6491	1211	N/A	5	1000	43	30	3000
2	Cement	4861	3934	1211	N/A	5	1000	43	30	3000
3	Cement	2576	2085	2422	N/A	5	1000	43	30	3000
4	Cement	4180	3383	1211	N/A	5	1000	43	30	3000
5	Cement	632	511	1557	N/A	5	1000	50	40	3000
6	Chemical	2576	2085	125.8	N/A	1000	500	43	30	3000
7	Cement	2917	2360	81.33333	N/A	5	1000	43	30	3000
8	Textile	1215	984	31.73333	N/A	150	N/A	50	40	3000
9	Textile	681	551	8.333333	N/A	150	N/A	50	40	3000
10	Cleaning	3451	2793	71.50556	75	100	50	43	30	3000
11	Cooling	4278	3462	300.2778	20	4.8	N/A	43	30	3000
12	Cleaning	3646	2951	12.55556	75	100	50	43	30	3000
13	Cleaning	1021	826	41.94444	75	100	50	50	40	3000
14	Cooling	5201	4209	200.0833	20	4.8	N/A	43	30	3000
15	Boiler	1944	1574	625	15	5	N/A	50	40	3000
			Freshwater quality					10	5	500

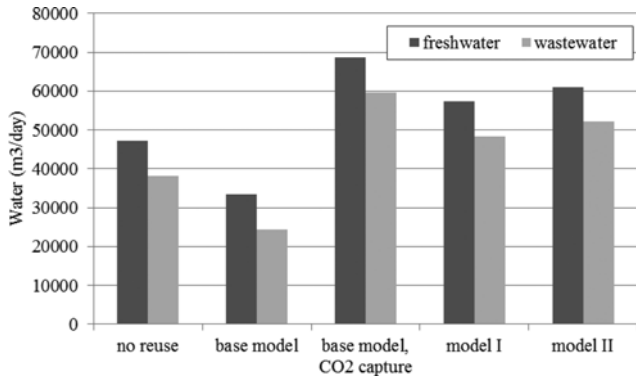

Fig. 14. Amount of freshwater usage/wastewater discharge for each model.

CO_2 emission reductions in this case. Figs. 15 and 16 represent the individual wastewater reuse network structures according to the different models.

CONCLUDING REMARKS

Hydrocarbons are a major contributor to economic development, but there are issues with climate change. To delay climate change, all sources of carbon dioxide must be estimated. To rigorously trace the total amount of emitted CO_2, direct carbon footprints and indirect embodied carbon should be traced, and their values should be computed. However, accurately estimating the entire emission amount is very difficult because many parts are outsourced, and detailed information is not available. CO_2 was considered in this paper in the context of direct operation, generating electricity, and carbon tax and emission certificates. When accurate data are available, the proposed model can be expanded.

The sustainable wastewater network problem can be also addressed in terms of cost analysis and sensitivity analysis; thus, accurate data for CCS and wastewater treatment are needed. Unfortunately, much of the data are not complete and under industry confidentiality. Instead of making unrealistic comparisons, this paper was concerned with constructing a decision-making framework to compute a sustainable water reuse network. The proposed framework helps to construct the network between wastewater supplies and demands based on the overall interactions of the model and data.

We incorporated the environmental impacts of CO_2 emissions for optimization of an industrial wastewater reuse network. CO_2 emissions from wastewater treatment as well as water consumption from carbon capture activity were introduced to the superstructure-based mathematical model. Material flow analysis was performed on an integrated iron and steel plant. As a case study, the water consumption changes due to energy/CO_2 emission reduction strategies were calculated in consideration of multiple contaminants and process units.

The results of the case study suggest that CO_2 emissions from wastewater can be an obstacle in the development of a wastewater reuse network. However, the problem is not so significant because (1) biological degradation was relatively low in the plants in both cases, and (2) the impacts of water consumption from the carbon capture facility outweighed the impact of indirect emissions. Additional water consumption of the system does not have a critical impact on CO_2/energy reduction, but reducing CO_2 and energy has a significant impact on water consumption. After a strategy is selected, water consumption can be problematic in operating utilities, and the capability of the proposed material flow model was proven in handling both issues of technology selection and water optimization simultaneously. The proposed methods can be used as industrial tools for handling large biological degradable waste-

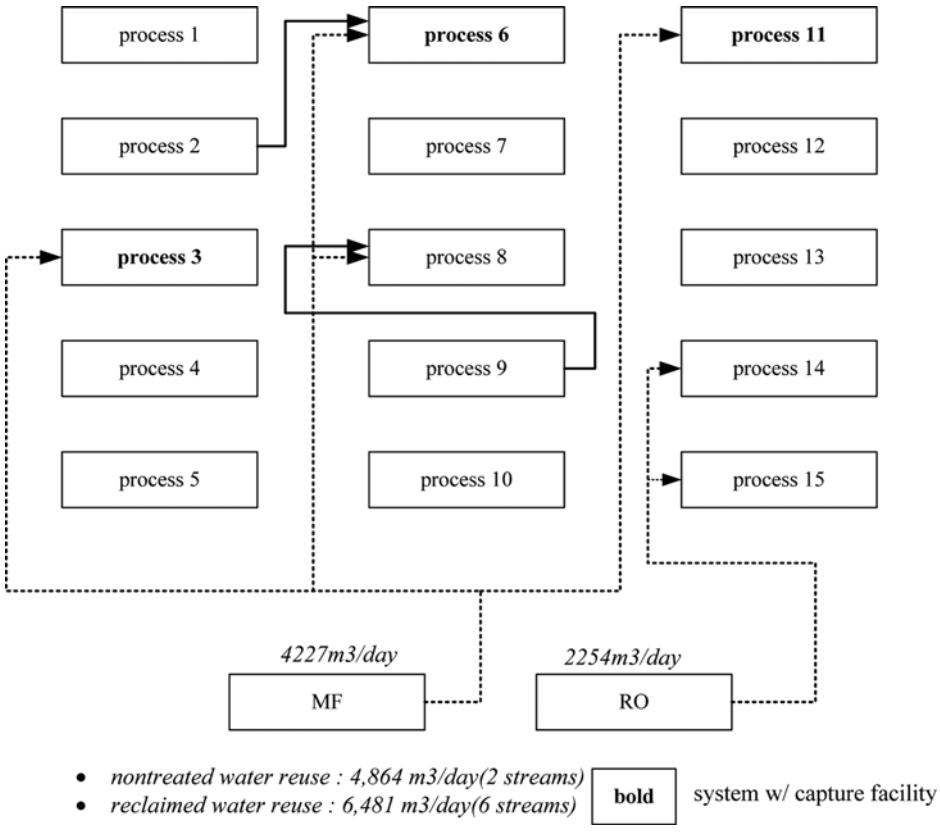

Fig. 15. Wastewater reuse network developed according to modified model I.

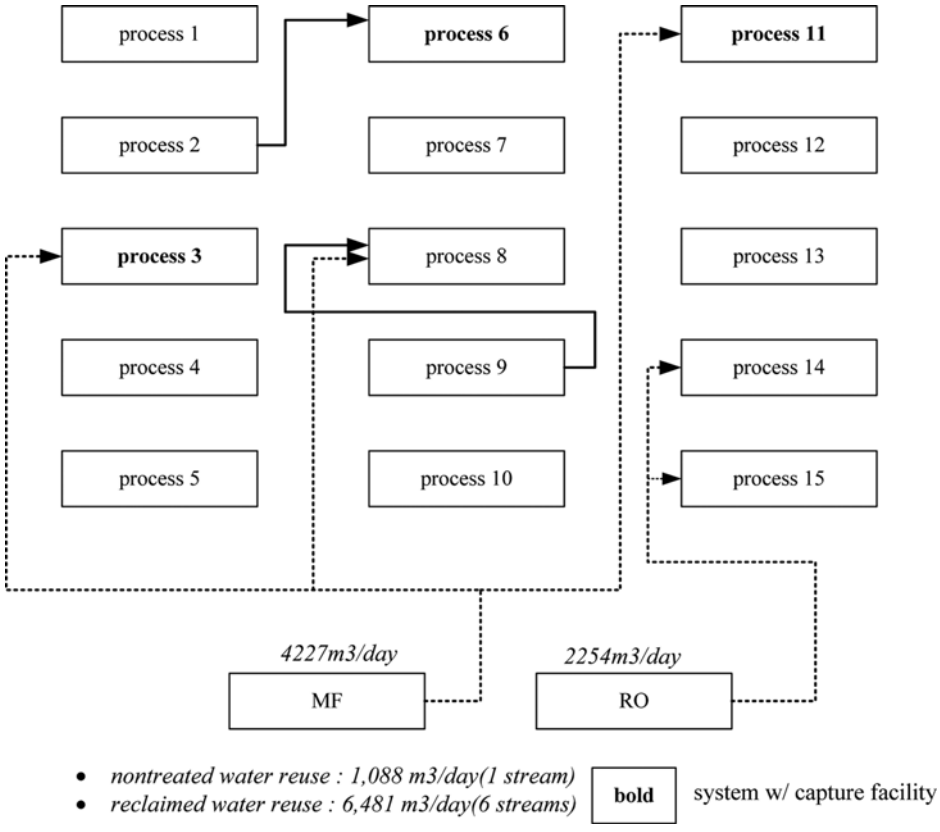

Fig. 16. Wastewater reuse network developed according to modified model II.

water, such as livestock production and agricultural industries. Related works are planned for constructing sustainable process environments based on environmentally friendly and economically desirable water reuse networks.

ACKNOWLEDGEMENTS

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NOMENCLATURE

Indices and Sets

i, j : water consuming unit
p, q : treatment unit
m, n : CO_2 capture facility
t : time index
f : $\in$[p, m]

Parameters

fw_i : freshwater [ton]
$bw_{j,i}$: untreated wastewater [ton]
$rw_{p,i}$: reclaimed water [ton]
cw_i : discharged to the surroundings [ton]
dfw : direct discharge water to the surroundings [ton]
tfw : total amount of freshwater needed in the system [ton]
tdw : total discharged wastewater [ton]
$trrw_{p,q}$: mixed into other treatment units reused in process units [ton]
$ptr_{a,x}$: the proportional treatment ability coefficient of the technology
$ptr_{b,x}$: a fixed outlet concentration of the second type of the facility [vol%]
$Crfw_x$: concentration of reclaimed freshwater x [vol%]
$Cfw_{i,x}$: concentration of freshwater input [vol%]
$Cbw_{j,i,x}$: concentration of untreated wastewater [vol%]
$Crw_{j,i,x}$: concentration of reclaimed wastewater [vol%]
$Cpwi_{i,x}^{low}$: lower bound Concentration of wastewater [vol%]
$Cpwi_{i,x}^{high}$: concentration upper bound of wastewater [vol%]
$Cdfw_x$: concentration of direct discharge water to the surroundings [vol%]
$Ctrfw_{p,x}$: concentration of total treated wastewater [vol%]
$Cpwo_{i,x}$: concentration of wastewater output [vol%]
$Cww_{i,p,x}$: concentration of wastewater [vol%]
$Ctwi_{p,x}$: concentration of x in water flowing into process p [vol%]
$Ctwo_{p,x}$: concentration of x in water discharging from process p [vol%]
$Ccw_{p,x}$: concentration of x in treated wastewater from treatment facility p [vol%]
$Ctrrw_{q,p,x}$: concentration [vol%] of x in water discharged from treatment process q to treatment process p
$Ctdw_x$: concentration [vol%] of x in total discharged wastewater
$Cdw_{i,x}$: concentration [vol%] of x in discharged water from process i
ε : a relatively small number
$trloss_p$: ratio of outlet water flowrate over inlet flowrate in process p
$Cdlimit_x^{low}$: minimum concentration limit of x in final wastewater [vol%]
$Cdlimit_x^{high}$: maximum concentration limit of x in final wastewater [vol%]
$price_{fw}$: price coefficient of freshwater [won/ton]
$price_{dw}$: wastewater discharge cost [won/ton]
$price_{rw}$: reclaimed water price [won/ton]
rwccsm, i : reclamined water CCS cost coefficient [won/ton]
$trcapital_p$: capital cost coefficient of wastewater treatment facility p [won/ton]
$troper_p$: operation cost coefficient of wastewater treatment facility p [won/ton]
S : a parameter denoting that capital cost of wastewater treatment facility is partially paid by external stakeholder; (S=0: the cost is solely paid by internal stakeholders)
pCO_{2m} : amount of CO_2 discharging from process m [$kgCO_2$]
$pcap_m$: capture ratio of CO_2 in process m
$p0CO_{2m}$: initial amount of CO_2 before treated in CCS facility [$kgCO_2$]
$pccsCO_{2m}$: amount of CO_2 in actually treated by process m [$kgCO_2$/t H20]
$p0ccsCO_{2m}$: amount of CO_2 flowing into process m [$kgCO_2$/t H20]
$ccscapa_m$: capacity of CCS in process m [$kgCO_2$]
CO_2limit_t : total CO_2 limit in time t [ton or ton equivalent]
$pipeCO_2$: amount of CO_2 emission in construction of wastewater transportation pipe [$kgCO_2$/tH2O]
$flow_t$: amount of flow at time t [ton]
$capcapital_m$: capital cost of carbon capture facility m [won/ton]
$capoper_m$: operation cost of carbon capture facility m
tax_t : price of tax in time t [won]
cer_t : price of certification in time t [won]
pipecost : pipe construction cost [won]
$constructCO_{2f}$: construction cost of CCS facility [won]

Variables

fw_i : freshwater consumption in process i [ton]
tfw : total freshwater consumption [ton]
pwi_i : wastewater input flow into process i [ton]
pwo_i : wastewater output flow from a process unit [ton]
$ww_{i,p}$: wastewater from process i to be treated in process p [ton]
dw_i : wastewater from process i discharging to the surrounding [ton]
$trfw_p$: total amount of freshwater consumption in process p [ton]
$trrw_{q,p}$: total amount of reclaimed water from process q to process p [ton]
cw_p : reclaimed water from process p discharging to the surrounding [ton]
$rw_{p,i}$: reclaimed water from process p to process i [ton]
twi_p : amount of water to be treated in process p [ton]
two_p : amount of water to be treated in process p [ton]
tCO_{2t} : basic CO_2 limit in time t [$kgCO_2$]
CO_{2m} : obtained CO_2 at CCS facility m [$kgCO_2$]
$taxCO_{2t}$: CO_2 tax refund in time t [won]
$cerCO_{2t}$: CO_2 certification purchase in time t [won]

tcost : total cost [won]

Binary Variables

$link_t$: binary variable denoting whether construction status is used at time t (1 if it is used, 0 otherwise)

$Ifacility_{f,t}$: binary variable denoting whether treatment facility or CCS facility is used (1 if used, 0 otherwise)

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