Abstract

Mass integration is a holistic approach to the optimal allocation, generation, and separation of streams and species. It addresses pollution using a combination of strategies including manipulation of process equipment, structural changes in the flowsheet, rerouting of streams and addition of new units. In the past, systematic mass integration techniques were developed to determine optimal strategies for the recycle and separation of process streams. The purpose of this paper is to introduce two novel contributions that can greatly expand the scope of mass integration for pollution prevention. First, maximum achievable pollution targets will be determined ahead of design and with little input data. In this context, we will illustrate the use of interval arithmetic to determine these targets. Second, pollution prevention through unit manipulation will be addressed. The devised interval-based targets possess the attractive feature that they are global regardless of the nonlinearity nature of the process model. These new concepts are illustrated with a case study. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Until recently, environmental solutions to processing facilities were in the form of end-of-pipe pollution control strategies. These are peripheral solutions that focus primarily on chemical, biological, and physical treatment of terminal streams. The result has been waste-treatment solutions that reduced the volume and toxicity of undesirable pollutants in industrial discharges. Although these pollution control strategies have resulted in reducing negative environmental consequences of processing facilities, they focused on the symptoms and not the true causes of the environmental problems. Therefore, they lacked cost-effectiveness and sustainability. It has been recently recognised that sustainable waste reduction must be based on an insightful pollution prevention that is founded on thorough understanding of the technical and economic issues of the process. This approach enables engineers to address the root causes of the environmental problems at the heart of the process. In this regard, mass integration provides a unique framework for addressing in-plant pollution prevention. Mass integration is a holistic approach to the generation, separation, and routing of species and streams throughout the process. It is a systematic methodology that provides a fundamental understanding of the global flow of mass within the process and employs this understanding in identifying performance targets and optimising the allocation, separation, and generation of streams and species. For recent literature on mass integration, the reader is referred to the textbook by El-Halwagi (1997) and the review article by El-Halwagi and Spriggs (1998).

The first step in conducting mass integration analysis is the development of a global mass allocation representation of the whole process from a species viewpoint as shown in Fig. 1. For each targeted species (e.g. each pollutant), there are sources (streams that carry the species) and process sinks (units that can accept the species). Process sinks include reactors, heaters coolers, biotreatment facilities, and discharge media. Streams leaving the sinks become, in turn, sources. Therefore, sinks are also generators of the targeted species.
Stream segregation and mixing provide additional design degrees of freedom that can be exploited to adjust flow rate and composition. In addition, each sink/generator may be manipulated via design and/or operating changes to affect the flow rate and composition of the sink generator accepts and discharges. Furthermore, properties of sources (e.g., flow rate, composition, pressure, temperature, etc.) can be modified by adding new units that intercept the streams prior to being fed to the process sinks and condition their properties to the desired values. This is performed in a waste interception network (WIN) (Garrison et al., 1995; El-Halwagi et al., 1996; El-Halwagi & Spriggs, 1996). Therefore, pollution prevention strategies include stream segregation/mixing, recycle, interception using separation devices, changes in design and operating conditions of units, materials substitution, and technology changes including the use of benign chemistry. These strategies can be classified into a hierarchy of three categories:

- No/low cost changes
- Moderate cost modifications
- New technologies

Three main factors can be used in describing these strategies, economics, impact, and acceptability. The economic dimension can be assessed by a variety of criteria such as capital cost, return on investment, net present worth, and payback period. Impact is a measure of the effectiveness of the proposed solution in reducing negative ecological and hazard consequences of the process, such as reduction in emissions and effluents from the plant. Acceptability is a measure of the likelihood of a proposed strategy to be accepted and implemented by the plant. In addition to cost, acceptability depends upon several factors including corporate culture, dependability, safety, and operability. Fig. 2 is a schematic representation of the typical hierarchy of pollution prevention strategies. These strategies are typically in ascending order of cost and impact and in descending order of acceptability. This paper will focus on process-related changes particularly low/no cost modifications and moderate cost changes involving unit addition/replacement. For issues and review literature on product design, material substitution and benign chemistry, and new green technologies, the reader is referred to Anastas and Farris (1994), Crabtree and El-Halwagi (1994), Joback (1994), Chase (1995), Achenie and Duvedi (1996), Anastas and Williamson (1996) and Hamad and El-Halwagi (1998). The following sections provide more details on strategies targeted in this paper.
2. Low/no cost strategies

These strategies can be broadly classified into two categories: structural and parametric modifications. The structure-based changes pertain to low/now cost in-process configuration such as stream rerouting (e.g. segregation, mixing, and recycle) which involves piping and pumping primarily. Systematic techniques have been developed to determine optimal segregation, mixing, and recycle strategies (e.g. Garrison et al., 1995; El-Halwagi et al., 1996; El-Halwagi & Spriggs, 1996; El-Halwagi, 1997). These techniques have also been extended to systems with multiple pollutants (Parthasarathy & El-Halwagi, 1997, 1999) and infinite components such as complex hydrocarbon mixtures (Shelley, Parthasarathy & El-Halwagi, 1998).

Parametric changes include moderate adjustments in equipment design variables (e.g. packing, baffles, nozzles) and operating conditions (e.g. temperature, pressure, etc.) which require modest or no capital expenditure. To date, these changes have not been incorporated into mass integration strategies and will be addressed by this paper.

3. Moderate cost changes

This category includes two main strategies: equipment addition and replacement, as well as material substitution. The following section is an overview of literature in both areas.

3.1. Equipment addition/replacement

Interception denotes the utilisation of new unit operations to adjust the composition, flowrate and other properties of the pollutant-laden streams to make them acceptable for existing process sinks. A particularly important class of interception device is separation systems. These separations may be induced by the use of mass separating agents (MSAs) and/or energy separating agents (ESAs). A systematic technique is needed to screen the multitude of separating agents and separation technologies to find the optimal separation system. The synthesis of MSA-induced physical-separation systems is referred to as the synthesis of mass-exchange networks (MENs) and has been introduced by El-Halwagi and Manousiouthakis (1989a). The subject of physical mass exchange networks has been addressed extensively in literature. This includes MENs with a single transferable component (El-Halwagi & Manousiouthakis, 1989a, 1990a), those with multiple transferable components (El-Halwagi & Manousiouthakis, 1989b), those involving regeneration of the MSAs (El-Halwagi & Manousiouthakis, 1990b), and mass exchange combined with heat exchange (Srinivas & El-Halwagi, 1994a,b), removal of fixed loads (Kiperstok & Sharratt, 1995), variable supply and target compositions (Garrison et al., 1995), fixed-cost targeting (Hallale & Fraser, 1997), MENs providing flexible performance (Papalexandri & Pistikopoulos, 1994; Zhu & El-Halwagi, 1995), controllable MENs (Huang & Edgar, 1995; Huang & Fan, 1995), and MENs with a single lean stream (water) with the objective of minimising water use (Wang & Smith, 1994; Dhole, Ramchandani, Tainsh & Wasilewski, 1996; Kuo & Smith, 1998).

Interception networks using reactive MSAs are termed reactive mass exchange networks (REAMEN) (El-Halwagi & Srinivas, 1992; Srinivas & El-Halwagi, 1994a,b).

Network synthesis techniques have also been devised for other separation systems that can be used in intercepting pollutants. These systems include pressure-driven membrane separations (e.g. Evangelista, 1986; El-Halwagi, 1992, 1993; Srinivas & El-Halwagi, 1993; Zhu & El-Halwagi, 1995), heat-induced separation networks (HISENs) (e.g. Dunn & El-Halwagi, 1994a,b; Dunn, Zhu, Srinivas & El-Halwagi, 1995; Dye, Berry & Ng, 1995; El-Halwagi, Srinivas & Dunn, 1995; Richburg & El-Halwagi, 1995; Dunn & El-Halwagi, 1994a,b; Dunn & Srinivas, 1997) and distillation sequences (e.g. Wachschauff, Jurian & Westerberg, 1991; Kovacs, Friedler & Fan, 1993; Malone & Doherty, 1995; Quesada & Grossmann, 1995).

4. Interval arithmetic

Driven by the need to estimate and control floating-point computational errors, the field of interval analysis has grown considerably over the past three decades. Consider a real variable, , which is bounded by two other numbers, . One can define an interval such that . One can define an interval such that . Similarly, an interval can be defined to include a real variable such that . Interval arithmetic is a mathematical approach that deals with the processing of intervals that bound real numbers. An interval arithmetic operation, (e.g. addition, subtraction, multiplication and division) is defined by

\[ X * Y = \{ x * y : x \in X, y \in Y \} \]  
(1)

A particularly useful property of interval arithmetic operations is

\[ x * y \subseteq X * Y \]  
(2)

which means that the sum, difference, product, and quotient of two real numbers belongs to the sum, difference, product, and quotient of the including intervals. Rules for interval operations include:

\[ X + Y = [x_l, x_u] + [y_l, y_u] = [x_l + y_l, x_u + y_u] \]  
(3a)
\[ X - Y = [x^i, x^u] - [y^i, y^u] = [x^i - y^i, x^u - y^u] \]  
(3b)

\[ X Y = [x^i, x^u][y^i, y^u] \]
\[ = \begin{cases} \min(x^i y^i, x^u y^u, x^i y^u, x^u y^i), \\ \max(x^i y^i, x^u y^u, x^i y^u, x^u y^i) \end{cases} \]  
(3c)

\[ X / Y = [x^i, x^u]/[y^i, y^u] = [x^i, x^u]/[1/y^u, 1/y^i] \]
if \(0 \neq [y^i, y^u]\)  
(3d)

Another useful property is the inclusion isotonicity of interval operations which states that for intervals \(X, Y, W\) and \(Z\)

if \(X \subset W\) and \(Y \subset Z\) then \(X^* Y \subset W^* Z\)  
(4)

For each continuous function, \(f(x)\) where \(x\) is an \(n\)-dimensional vector and \(x \in X\), one can use interval arithmetic to identify bounds on the range of the function. Consider a function \(f(x)\) whose range over interval \(X\) is defined as \(\Box f(X)\), i.e. \(\Box f(X) = \{f(x) : x \in X\}\). An interval function \(F\) is called an inclusion function for \(f\) over interval \(X\) if

\[ \Box f(X) \subseteq F(X) \]  
(5)

Inclusion functions are extremely important in interval analysis as they provide bounds on ranges without exhaustive enumeration. There are two common methods for constructing inclusion functions: natural interval extensions and centred forms. A natural interval extension is an expression in which the each \(x\) in the various terms of \(f(x)\) is replaced with its including interval \(X\) and the mathematical operators are replaced with interval operations. Centred forms are inclusion functions which represent generalisation of the algebraic centred forms for real variables. A particularly useful centred form is based on the natural interval extension of Taylor's expansion of the function. For more details on interval analysis, the reader is referred to Ratschek and Rokne (1984a,b), Moore (1988).

5. Targeting

Prior to undertaking extensive design and optimisation computations, it is beneficial to identify bounds on performance. In this regard, targeting is a powerful design technique. It enables the designer to determine performance criteria of the system ahead of detailed design and without commitment to the final configuration(s) of proposed solution alternatives. Targeting has been successfully used in various elements of process integration such as the identification of minimum heating and cooling utilities for heat exchange networks (e.g. Linhoff & Hindmarsh, 1983), minimum cost of mass separating agents (e.g. El-Halwagi & Manousiouthakis, 1989a,b), and minimum flowrate of wastewater (e.g. Wang & Smith, 1994; El-Halwagi, 1997; Kuo & Smith, 1998). These targeting techniques have capitalised on the use of composite representations for the system. They are also based on fundamental thermodynamic and economic principles. The rules applied in these targeting procedures are generally applicable to the defined systems and have provided significant insights into the integrated nature of the processes. In the context of pollution prevention, the development of targeting techniques is critically needed as a staggering number of processing companies are examining their pollution prevention potential.

6. Scope and objectives

Let us raise the following fundamental question: what is the target for preventing pollution from a processing facility? The answer is simple and promising; discharge of targeted pollutants to the environment can be virtually eliminated, thereby allowing the process to approach a zero-discharge target. To justify this answer, we should recall the various pollution prevention strategies represented by Fig. 2. In principle, it is possible to approach this zero-discharge target by one or more of the following options:

1. The targeted species can be completely replaced from the process. Examples include:
   - Use of alternate reaction routes that do not involve the targeted species.
   - Substitution of materials (e.g. solvent substitution when the original solvent is the targeted species).

2. Technology can be changed to avoid the involvement of the targeted species. Examples include:
   - Dry processing instead of wet processing to avoid the use of water and the generation of wastewater.
   - Solvent-free processing (e.g. solvent-less coating, condensation instead of absorption).

3. Sharp separations can be applied to terminal and in-plant streams to remove targeted species from discharges. Even if the separation system is not highly efficient, it is conceivable that they can be staged to reach progressively smaller compositions in the effluent streams. For instance, consider an organic pollutant in flue gases. In principle, it is possible to use a series of selective adsorption columns that will eventually get the final discharge below detection limits.

4. Reactive methods (chemical and biological) can be used to detoxify the pollutants or convert them to salable/reusable species. Again, staging can be used to reach significantly small concentration levels.

The foregoing discussion illustrates that indeed zero-discharge targets can be approached and designed for. The techno-economic feasibility of achieving this target depends on the state-of-the-art in pollution prevention
techniques and the continuous progress in research and development over the next few decades. Nonetheless, processing facilities are interested in more focused questions and targets that pertain to their current and near-future environmental performance. In particular, there is a great need to identify targets for the following cases:

1. What is the maximum capability of the existing process to prevent pollution without adding new equipment? A key limitation in current literature is the lack of targeting techniques to incorporate potential changes in design and operating variables. This is a critical need since most pollution prevention strategies involve the simultaneous manipulation of operating conditions (e.g. temperature, pressure, residence time) as well as design modifications (e.g. intra-unit changes).

2. If the plant does not wish to replace or eliminate the use of the targeted species, what is the target for preventing pollution to the environment? This situation is commonly encountered in the use of preferred feedstocks and material utilities (e.g. raw materials, water, solvents, blanketing gases) that eventually become waste streams (e.g. unreacted raw materials, wastewater, gaseous emissions) but the plant wishes to continue to use them. The situation is further compounded by the need to recycle/reuse unreacted raw materials and spent material utilities to replace fresh purchases, conserve resources, and provide a more integrated process.

The identification of targets for these two categories is the primary goal of this work. These targeting techniques will be developed using a combination of mass integration and interval analysis particularly inclusion principles. The devised procedures will be illustrated by a case study.

7. Problem statement

The problem to be addressed in this paper can be stated as follows: given a process with terminal gaseous and liquid wastes which contain certain pollutants, it is desired to identify targets for reducing waste discharge for the following two categories:

1. Pollution is prevented by manipulating design and operating degrees of freedom for existing process equipment.

2. Targeted species are feedstocks and material utilities that can be reused in the process using structural changes such as stream rerouting and interception as well as manipulation of design and operating degrees of freedom for existing process equipment.

The problem can be more formally stated as follows: Given a process which disposes of a set $T$ of terminal wastes: $\text{TERMINAL} = \{i | i = 1, 2, \ldots, N_{\text{Terminal}}\}$ containing a set of undesirable species $K = \{k | k = 1, 2, \ldots, N_{\text{components}}\}$. The flowrate of each terminal waste, $W_i$, and its discharge composition, $Z_i$, are given. Throughout the plant, there is a set of pollutant-laden streams, referred to as SOURCES = $\{i | i = 1, N_{\text{sources}}\}$. This set includes in-process streams as well as terminal wastes. These sources are processed through or can be fed to a set SINKS = $\{s | s = 1, N_{\text{sinks}}\}$ of process units and is a subset of the total flowsheet. Each sink has a set of input streams and a set of output streams, INPUT, and OUTPUT, respectively. In order to feed a stream to a unit, it must satisfy the range of acceptable flowrate and composition of the sink, i.e.

$$G_{j}^{\text{min}} \leq G_j \leq G_{j}^{\text{max}} \quad j \in \text{INPUT}, \quad s \in \text{SINKS} \quad (6)$$

$$y_{j,k}^{\text{min}} \leq y_{j,k} \leq y_{j,k}^{\text{max}} \quad j \in \text{INPUT}, \quad s \in \text{SINKS}, \quad k \in K \quad (7)$$

There is also a set FRESH = $\{j | j = 1, N_{\text{Fresh}}\}$ of fresh sources entering the process while carrying the targeted species. This is a subset of all input streams entering process sinks.

For the $s$th sink, $d_s$ and $p_s$ designate the vectors of design and operating degrees of freedom that can be manipulated and optimised. The intervals of all permissible values of design and operating degrees of freedom for the $s$th sink are designated as $D_s$ and $P_s$ such that $d_s \in D_s$ and $p_s \in P_s$. Examples of $d_s$ include structural decisions such as increasing surface area, adding/replacing internals such as packing, trays and baffles, etc. Examples of $p_s$ include operating conditions that can be altered for existing equipment such as temperature, pressure, catalyst turn-over rates, motor speed, etc.

It is desired to identify a target on discharged amount of the targeted species for the following two classes of problems:

1. Pollution is prevented by manipulating design and operating degrees of freedom for existing process equipment ($d_s$ and $p_s$ where $s \in \text{SINKS}$).

2. Targeted species are feedstocks and material utilities that can be reused in the process using structural changes such as stream rerouting and interception as well as manipulation of design and operating degrees of freedom for existing process equipment.

8. Solution strategy

In order to address the aforementioned problem, we will employ various useful concepts. First, we extend the notion of a path-diagram to include potential changes in the design and operation. Next, we use interval arithmetic to provide bounds on pollution prevention targets. Finally, we employ mass integration strategies to attain these targets.
In this paper, we extend its scope to include design and targeted species are excluded. To date, the path equations simulate the input–output relations of selected units and sinks, it is necessary to use an analytical tool that tracks the flow and composition of the specific targeted species throughout the process. It is an analytical tool that tracks the flow and composition of the specific targeted species throughout the process through material balances and unit modelling equations. Units and streams that do not involve the targeted species are excluded. To date, the path equations and its graphical analogue the path-diagram (Garrison et al., 1995; El-Halwagi et al., 1996). It is an analytical tool that tracks the flow and composition of the specific targeted species throughout the process through material balances and unit modelling equations. Units and streams that do not involve the targeted species are excluded. To date, the path equations have focused on output presentations rather than input presentations. In this paper, we extend its scope to include design and operating variables.

Consider a sink, s, which has the set INPUTs of streams entering the unit and the set OUTPUTs of streams leaving the unit. Gs and Ws are the flowrates of the jth and ith sources entering and leaving the unit. Their kth-component compositions are denoted by yjk and zk,k, respectively, where k ∈ K. As a result of chemical reaction, fugitive emissions, and loss in streams that are not classified as wastes (e.g. products and unregulated by-products), the net depletion of species k in unit s is denoted by Netk,s (negative in case of net generation). (Fig. 3)

In any sink, s, the input/output relations depend not only on the entering and exiting flowrates and compositions, but also on design and operating variables. While some of these variables are fixed by process objectives such as product quality, throughput, safety, maintenance and controllability, other variables are classified as degrees of freedom to be manipulated so as to achieve the pollution prevention targets. These are the vectors ds and ps defined earlier in the problem statement. They represent design and operating degrees of freedom that can be manipulated and optimised for the 8th sink. The problem statement has also defined the intervals of all permissible values of design and operating degrees of freedom as Ds and Ps, respectively. Hence, the input/output path relationship for the 8th sink can be expressed as: Unit performance expressions:
Let us define the following two terms:

\[ k_i \]

A schematic representation of this overall balance is shown by Fig. 4.

We are now in a position to identify a target on discharged amount of the targeted species for the two classes of problems defined in the problem statement.

10. Category I: targeting for sink/generator manipulation

In many cases, a plant wishes to identify how far pollution can be prevented by capitalising on existing equipment only while allowing changes in operating and design degrees of freedom for the various units (e.g. altering temperature and pressure, replacing one type of packing with another or replacing trays with packing, etc.). As described by Fig. 2, this is typically one of the first pollution prevention strategies that are highly acceptable, low in cost and modest in impact. We will refer to this strategy by sink/generator manipulation SGM. Let us now establish a pollution prevention target for this strategy. Towards this end, we carry out interval computations for Eqs. (12)–(15), the path inclusion, over intervals \( D_i \) and \( P_i \), to evaluate the inclusion of \( \text{TERMINAL}_k \text{LOAD}_k \text{SGM} \), \( \text{FRESH}_k \text{LOAD}_k \text{SGM} \), \( \text{FORBIDDEN}_k \text{LOAD}_k \text{SGM} \) and \( \text{Net}_k \text{process}_k \text{SGM} \). Therefore, the inclusion of Eq. (20) can be rewritten as:

\[
\text{TERMINAL}_k \text{LOAD}_k \text{SGM} = \text{FRESH}_k \text{LOAD}_k \text{SGM} - \\
\text{Net}_k \text{process}_k \text{SGM} k \in K
\]

where

\[
\text{TERMINAL}_k \text{LOAD}_k \text{SGM} = [\text{TERMINAL}_k \text{LOAD}_k \text{SGM}, I] , \\
\text{TERMINAL}_k \text{LOAD}_k \text{SGM}, u]
\]
With the target for terminal load discharge under all possible sink/generator manipulations being TERMINAL\_LOAD\_SGM, as it constitutes a lower bound on all possible values of TERMINAL\_LOAD\_k for all permissible values of design and operating degrees of freedom, i.e. \( d_i \in D_i \) and \( p_j \in P_j \). Fig. 5 illustrates the overall material balance after sink/generator manipulation. At this stage of targeting, some observations are warranted:

1. The identified target is a global one regardless of the non-linearities involved in the process. Bounding characteristics and inclusion isotonicity of interval analysis are independent of the type of non-linearities and non-convexities of the system. This is extremely important in comparison to optimisation approaches whose results can be comparable only when the (often evasive) global solution is identified.

2. The inclusion computations are carried out one time only to evaluate the target, TERMINAL\_LOAD\_SGM, over all possible variations of design and operating changes belonging to intervals \( D_i \) and \( P_j \). Therefore, the combined effects of varying all degrees of freedom can be obtained without any trial-and-error or enumerative computations.

3. The tightness of the interval TERMINAL\_LOAD\_k SGM (compared to real-number evaluations) depends on the method of interval inclusions. Typically, centred forms are tighter than natural inclusions.

4. The rigor of the target depends on the accuracy of the modelling (path Eqs. (8) and (9)). While the target is rigorous for the developed path equations, model-plant mismatches can influence the rigor of the target for the actual-plant. Interestingly enough, interval analysis can be used to quantify the maximum deviation between the modeled target and the actual-plant target. This can be achieved by rewriting Eqs. (12) and (13) to include model uncertainty. The difference between the target with and without model uncertainty indicate how sensitive the target is to model accuracy. It also sheds insightful light on appropriate level of modeling for a process integration study.

11. Category II: targeting for feedstocks and material utilities with recycle and interception

In this category, targeted species are feedstocks and material utilities that can be reused in the process. Examples include raw materials, water, solvents, fuels, and blanketing gases. These materials are eventually turned into spent streams (e.g. unreacted raw materials, wastewater, volatile organic compounds, flue gases) that can be partly or completely reintroduced into the process to alleviate environmental impact and reduce the purchase of fresh resources. To allow reutilization of the spent material utilities, we can use a combination of structural changes such as stream rerouting and interception (e.g. separation devices that can adjust flow-rates and compositions) as well as manipulation of design and operating degrees of freedom for existing process equipment.

It is worth pointing out that not all terminal streams are amenable to recycle/reuse or processing. This can be attributed to reasons that are technical (e.g. a species in recycled streams may compromise product quality), environmental (e.g. when certain species are reused, special hazardous materials permits are required), safety (there is an unacceptable probability that process safety may be compromised if certain species are reintroduced into the process), perception (e.g. the corporate culture has not allowed certain types of recycle and do not wish to go down this path), and economic (e.g. it is conspicuous even ahead of mass integration analysis that certain strategies are economically unfeasible; for instance, recovery of parts per trillion of a solvent from water, recovery of water from flue gas, etc.). As a result, one can define a set of streams that are not to be included in the investigation of recycle, reuse, and interception. This set is denoted by FORBIDDEN = \( \{ i \mid i \in \text{TERMINAL}, i \text{ cannot be recycled, reused or intercepted} \} \). The rest of terminal streams constitute another set called RECYCLABLE and is defined as RECYCLABLE = \( \{ i \mid i \in \text{TERMINAL} \text{ and } i \text{ can be recycled, reused or intercepted}\} \). Therefore, we can define the following loads:

\[
\text{FORBIDDEN\_LOAD}_k = \sum_{i \in \text{FORBIDDEN}} W_i Z_{i,k} \quad (24)
\]

and

\[
\text{RECYCLABLE\_LOAD}_k = \sum_{i \in \text{RECYCLABLE}} W_i Z_{i,k} \quad (25)
\]

Therefore, it follows that

\[
\text{TERMINAL\_LOAD}_k = \text{RECYCLABLE\_LOAD}_k + \text{FORBIDDEN\_LOAD}_k \quad (26)
\]

Within the current category of problem statement, we will address two cases.
11.1. Net generation/depletion of the targeted species is independent of stream rerouting activities

Let us first consider the case where the net generation/depletion of the targeted species is independent of stream rerouting activities. In this case, the term Net_process^k is indifferent to any changes in stream allocation. Examples of this case are:

Intervals defined by constraints Eqs. (6) and (7) have narrow widths. Hence, any recycled stream (with or without interception) must have flowrate, composition, and other properties that are almost identical to the original stream fed to the unit. Therefore, after recycle, the performance of units involving net generation/depletion will remain the same as it was before recycle.

When net generation/depletion of units is insensitive to the constraints Eqs. (6) and (7). This insensitivity can be assessed by evaluating the interval inclusion of the term Net^s,k for each unit s when inputs to units are allowed to vary within the intervals defined by constraints Eqs. (6) and (7).

The term Net_process^k is much smaller than the terms Terminal_Load^SGM and Fresh_Load^k. An example of this case is encountered when the net generation/depletion by reaction systems is a minor contributor to the overall load of pollutants in terminal streams.

In this case, reduction in terminal load is critically dependent on reduction in fresh load. Indeed, as can be seen from Eq. (20), for each unit mass reduction in fresh load there is an equal reduction in terminal load. In addition to sink/generator manipulation addressed in the previous section, there is an additional way to reduce fresh load. This can be achieved by replacing fresh usage of the targeted species with recycled species from terminal streams. In principle, it is possible to replace any fresh source of the targeted species with an equivalent amount of recycle from a terminal or an in-process stream. If the composition and flowrate of the recycled stream meets constraints Eqs. (6) and (7) for units employing fresh sources, then we can undertake direct recycle from those terminal streams to those units employing fresh sources. On the other hand, if flowrate and/or composition constraints are not met, then the terminal streams must be intercepted to render them in a condition that allows replacement of fresh sources. It is important to note that these recycle activities should be limited to rerouting terminal streams (with or without interception) to units that employ fresh resources. In order to illustrate this observation, let us consider the process shown in Fig. 6. In this process, three fresh streams (j = 1–3) carry the targeted species. The required input load of the kth targeted species in these streams is denoted by Fresh_Load^k,i.

Let us first consider recycle from terminal streams to units that do not employ fresh resources. For instance, as shown by Fig. 7a, let us recycle a load of R^k,2 from the inlet of unit # 5 and a load of R^k,1 from j = 2 to the inlet of unit # 4. Since we are dealing with the case where recycle activities have no effect on Net_process^k, the loads in the individual terminal streams are simply redistributed with the total terminal load remaining the same (Terminal_Load^k,1 + Terminal_Load^k,2 + Terminal_Load^k,3 + Terminal_Load^k,4).

This observation can also be deduced from Eq. (20) by noting that since the fresh loads entering the process remain constant, and since this case deals with unaffected Net_process^k, the total terminal load will remain the same. Therefore, in this case, sinks that do not employ fresh sources of the targeted species are poor destinations for recycle.
Next, we consider recycles that reduce fresh loads. For instance, let us examine the effect of recycling a load of \( R_{k,1} \) from \( i = 1 \) to the inlet of unit \# 2 and a load of \( R_{k,2} \) from \( i = 2 \) to the inlet of unit \# 1. This is shown by Fig. 7b. The result of the fresh source replacement is a net reduction of \( R_{k,1} + R_{k,2} \) from \( \text{FRESH LOAD}_k \) and consequently (and consistent with Eq. (20)) the total terminal loads are reduced by \( R_{k,1} + R_{k,2} \). It is worth noting that these appropriate recycles are not limited to terminal streams. Instead, what is needed is the replacement of fresh loads with recycled loads from an in-plant or a terminal source. For example, the same effect shown in Fig. 7b can be accomplished by recycling (with or without interception) from in-plant sources (e.g. \( i = 5 \)) as shown in Fig. 7c.

The foregoing discussion illustrates that in the case where the net generation/depletion of the targeted species is independent of stream rerouting activities, replacement of fresh sources with recycled sources, reduces the term \( \text{FRESH LOAD}_k \) and (according to Eq. (20)) also reduces \( \text{TERMINAL LOAD}_k \). Therefore, the higher the replacement, the lower the terminal discharge. The maximum amount of targeted species \( k \) that can be recycled from terminal streams to replace fresh sources is limited by the lower of the two loads, i.e.

\[
\text{Maximum replaceable load in fresh sources} = \min \left( \text{FRESH LOAD}_k, \text{TERMINAL LOAD}_k \right) \quad k \in K
\]

(27)

Therefore, for this category the target can be identified by performing inclusion calculations for the path-diagram over intervals \( D_k \) and \( P_k \), evaluating the resulting intervals for \( \text{TERMINAL LOAD}_k \) and comparing with \( \text{FRESH LOAD}_k \), according to Eq. (27) to determine the maximum extent for recycle. The unrecycled load will then constitute the target.

It is worth pointing out that if the targeted species cannot be rerouted from streams that are forbidden from recycle to streams that are recyclable, then less loads can be recycled to replace fresh sources and Eq. (27) becomes: Maximum recyclable load for species \( k \)

\[
k = \min \left( \text{FRESH LOAD}_k, \text{RECYCLABLE LOAD}_k \right) \quad k \in K
\]

(28)

In this case, the target can be identified by performing inclusion calculations for the path-diagram over intervals \( D_k \) and \( P_k \), evaluating the resulting intervals for \( \text{RECYCLABLE LOAD}_k \) and comparing with \( \text{FRESH LOAD}_k \) according to Eq. (28) to determine the maximum extent for recycle. The unrecycled load will then constitute the target.

It is worth pointing out that the following interesting cases may be encountered:

\[
\text{RECYCLABLE LOAD}_k \geq \text{FRESH LOAD}_k^l \quad (29)
\]

where the superscripts \( l \) and \( u \) refer to the lower and upper bounds of evaluated intervals.

According to Eq. (28), we can only recycle a load of \( \text{FRESH LOAD}_k^l \) leaving us with a target for net terminal discharge being \( \text{RECYCLABLE LOAD}_k^l - \text{FRESH LOAD}_k^l \). This is the case of zero purchase of fresh targeted species.

On the other hand, if

\[
\text{RECYCLABLE LOAD}_k^u \leq \text{FRESH LOAD}_k^l \quad (30)
\]

Then according to Eq. (28), we can fully reuse the recyclable terminal streams leaving us with a zero-discharge target for the recyclable terminal streams and a target on the net purchase of fresh resources of \( \text{FRESH LOAD}_k^l - \text{RECYCLABLE LOAD}_k^u \).

11.2. Net generation/depletion of the targeted species is dependent on stream rerouting activities

As a result of sink/generator manipulation, recycle and interception, the various flowrates and compositions may change. However, they should be allowed to vary only within the intervals defined by constraints Eqs. (6) and (7). Therefore, regardless of the extent of sink/generator manipulation, recycle and interception, constraints Eqs. (6) and (7) include all feasible inputs to the units. Hence, we can now carry out the interval computations for Eqs. (12)–(15) over intervals Eqs. (6) and (7), \( D \) and \( P \), to obtain the inclusion of \( \text{TERMINAL LOAD}_k \), \( \text{FRESH LOAD}_k \), and \( \text{Net process}_k \) along with Eq. (27) or Eq. (28) can be used to evaluate the maximum extent of recycle and hence identify the target as in the previous case. Again, this is a one-time calculation that can evaluate the target for minimum discharge.

In order to demonstrate the devised targeting procedure, let us consider the following case study.

12. Case study: reduction of water usage and discharge in a tire-to-fuel plant

This case study is adapted from El-Halwagi (1997). It involves a processing facility that converts scrap tires into fuel via pyrolysis. Fig. 8 is a simplified block flow diagram of the process. The discarded tires are fed to a high-temperature reactor where heat breaks down the hydrocarbon content of the tires into oils and gaseous fuels. The oils are further processed and separated to yield transportation fuels. As a result of the pyrolysis reactions, water also is formed. The amount of generated water is a function of the reaction temperature, \( T_{\text{ran}} \), through the following correlation:
$W_{\text{rxn}} = 0.152 + (5.37 - 7.84 \times 10^{-3} T_{\text{rxn}}) e^{(27.4 - 0.04 T_{\text{rxn}})}$

(31)

Where $W_{\text{rxn}}$ is in kg/s and $T_{\text{rxn}}$ is in K. At present, the reactor is operated at 690 K which leads to the generation of 0.12 kg water/s. In order to maintain acceptable product quality, the reaction temperature should be kept within the following range:

$690 \leq T_{\text{rxn}}(K) \leq 740$

(32)

The reactor off-gases are cooled to condense light oils. The condensation is decanted into two layers: aqueous and organic. The aqueous layer is a wastewater stream which contains phenol as the primary pollutant. The flow rate of this wastewater stream is designated as $W_1$. The organic layer is mixed with the liquid products of the reactor, and fed to finishing. A gaseous waste leaves the finishing unit and is flared. To prevent the back-propagation of fire from the flare, a seal pot is used. An aqueous stream whose flowrate is $G_2$ is passed through the seal pot to form a buffer zone between the fire and the source of the flare gas. To avoid accumulation of impurities in the seal pot, an equivalent flowrate of wastewater stream, $W_2$, is withdrawn from it.

Tire shredding is achieved by using high-pressure water-jets. The shredded tires are fed to the process while the spent water is filtered. The wet cake collected from the filtration system is forwarded to solid waste handling. The filtrate is mixed with fresh water-jet makeup $G_1$ to compensate for water losses with the wet cake $W_3$ and the shredded tires. The mixture of filtrate and water makeup is fed to a high-pressure compression station for recycle to the shredding unit. The flowrate of water-jet makeup depends on the applied pressure coming out of the compression stage $P_{\text{comp}}$ via the following expression:

$G_1 = 0.47e^{-0.009 P_{\text{comp}}}$

(33)

where $G_1$ is in kg/s and $P_{\text{comp}}$ is in atm. In order to achieve acceptable shredding, the jet pressure may be varied within the following range:

$70 \leq P_{\text{comp}}(\text{atm}) \leq 90$

(34)

At present, $P_{\text{comp}}$ is 70 atm which requires a water-jet make-up flowrate of 0.25 kg/s. The water lost in the cake is related to the mass flowrate of the water-jet makeup through: $W_3 = 0.4 G_1$.

In addition to the water in the wet cake, the plant has two primary sources for wastewater; from the decanter ($W_1$) and from the seal pot ($W_2$). At present, the values of $W_1$, $W_2$, and $W_3$ are 0.27, 0.15, and 0.10 kg/s, respectively. The wastewater from the decanter contains about 500 ppm of phenol. Within the range of allowable operating changes, this concentration can be assumed to remain constant. At present, the wastewater from the seal pot contains no phenol. The plant has been shipping the wastewater streams $W_1$ and $W_2$ for off-site treatment. The cost of wastewater transportation and treatment is $0.10/kg leading to a wastewater treatment cost of approximately $1.33 million/year. $W_3$ has been processed on site. Because of the characteristics of $W_3$, the plant does not allow its recycle back to the process even after waste handling processing (a forbidden stream). The plant wishes to reduce (or if possible to stop) off-site treatment of wastewater streams $W_1$ and $W_2$ to avoid cost of off-site treatment.
and alleviate legal-liability concerns in case of transportation accidents or inadequate treatment of the wastewater. The objective of this problem is determine a target for reduction in flowrate of terminal discharges $W_1$ and $W_2$. Fig. 9 shows an overall water balance for the process before mass integration.

### 13. Solution

The first step in the analysis is to identify the target for reducing terminal wastewater flowrate by sink/generator manipulation. Two degrees of freedom are available: reaction temperature and compression pressure. The intervals for permissible values of these two variables are given by Eqs. (32) and (34). The path equations for the process are given by:

\[
W_1 + W_3 = G_1 + \text{Net}\_\text{process}\_\text{water} \tag{35}
\]

\[
W_3 = 0.4 \times G_1 \tag{36}
\]

\[
W_2 = G_2 \tag{37}
\]

\[
G_2 = 0.15 \tag{38}
\]

\[
\text{Net}\_\text{Process}\_\text{water} = 0.152
\]

As mentioned earlier, the two operating conditions that can be manipulated are $P_{\text{comp}}$ and $T_{\text{rxn}}$ with the permissible intervals being $[70, 95 \text{ atm}]$ and $[690, 740 \text{ K}]$, respectively. Therefore, by carrying out interval inclusion for the path equations over these two intervals, we get the lower bounds for $W_1$, $W_2$, and $W_3$ to be 0.20, 0.15, and 0.08 kg/s, respectively, with the lower bound on the TERMINAL\_LOAD\_water being 0.43 kg/s. These lower bound results are shown in Fig. 10 and represent the target for water discharge after sink/generator manipulation with existing units and current process configuration.

Next, we consider recycle and interception. We can employ the case where the net generation/depletion of the targeted species is independent of stream rerouting activities. Therefore, by performing inclusion calculations for the path-diagram over the intervals $[70, 95 \text{ atm}]$ and $[690, 740 \text{ K}]$ for $P_{\text{comp}}$ and $T_{\text{rxn}}$, we get $\text{RECYCLABLE}\_\text{LOAD}_f$ to be 0.35 kg/s and $\text{FRESH}\_\text{LOAD}_f$ to be also 0.35 kg/s. Hence, we can close the water loop by having zero-discharge for $W_1$ and $W_2$ while eliminating the fresh water completely. This is a special case of Eqs. (29) and (30) where both zero-discharge and zero purchase of fresh resource can be achieved. This target is shown in Fig. 11.

Although beyond the scope of this paper, it is instructive to employ mass integration strategies to achieve this target. Optimisation-based techniques (El-Halwagi et al., 1996; El-Halwagi, 1997) as well as graphical tools (El-Halwagi & Spriggs, 1996; El-Halwagi, 1997) can be used to develop a specific cost-effective solution for the identified target. The development of this solution is given in the Appendix and the final
solution is shown by Fig. 12. It involves the increase of reaction temperature to 710 K and the increase of compression pressure to 95 atm. The solution also includes direct recycle from the decanter to the seal pot and an intercepted recycle (using stripping) from the seal pot to the compression station.

14. Conclusions

This work has presented a systematic framework for identifying pollution prevention targets ahead of detailed design. Interval analysis and mass integration were employed to establish bounds on maximum extent of reducing terminal discharges. In particular, two important classes of problems were considered. In the first category, targets were identified for pollution prevention by manipulating design and operating degrees of freedom for existing process equipment. This is an indication of the inherent capability of the process to prevent pollution. In the second category, targeted species included feedstocks and material utilities that can be reused in the process using structural changes such as stream rerouting and interception as well as manipulation of design and operating degrees of freedom for existing process equipment. Rigorous targets were also identified for terminal discharge as well as fresh purchases. The devised interval-based targeting procedures offer several merits. They are rigorous without computational intensity. A one-time computation is needed to bound the target. Furthermore, the identified targets are guaranteed for globality regardless of the nonlinear nature of the system. Therefore, they offer significant advantages over optimization-based approaches. If the identified target is promising, then effort can be made to use detailed mass integration strategies to identify specific cost-effective solutions that attain the target.

15. Nomenclature

- $C$: cost of MSA, $/kg MSA$
- $d_s$: vector of design degrees of freedom
- $D_s$: permissible values of design degrees of freedom
- $f(x)$: function of vector $x$
- $f(X)$: inclusion of function $f$ over interval $X$
- FORBIDDEN: set of terminal streams that cannot be recycled
- FORBIDDEN_: defined by Eq. (24)
- LOAD$_s$: set of fresh inputs to the plant
- FRESH$_k$: load of the $k$th species entering the process as defined by Eq. (19)
- $G_j$: flowrate of the $j$th sources entering the unit
- $G_j^{\text{max}}$: maximum flowrate of the $j$th inlet to the unit
- $G_j^{\text{min}}$: minimum flowrate of the $j$th inlet to the unit
- $I$: index for set SOURCES and subset TERMINAL
- INPUT$_s$: set of input streams
- INPUT$_{st}$: set of input streams to the $s$th sink
$
J$  
index for set SINKS

$K$  
index for components set $K$

$M$  
Slope of equilibrium line

$N_{:\text{component}}$  
total number of target species

$N_{:\text{fresh}}$  
total number of fresh sources

$N_{:\text{sinks}}$  
total number of sinks species

$N_{:\text{sources}}$  
total number of sources

$\text{Net}_{i,k}$  
net rate of depletion and losses of the $k$th component in the $i$th unit

$N_{:\text{terminal}}$  
total number of terminal species

OUTPUT  
set of output streams

$\text{OUTPUT}_s$  
set of output streams from the $s$th sink

$P_S$  
vector of operating degrees of freedom

$P_{comp}$  
pressure of compression station

$P_{SGM}$  
interval for permissible values of operating degrees of freedom

$R_{s,1}$  
$k$th-component load recycled from the $i$th source

RECYCLABLE  
set of terminal streams that can be recycled

RECYCLABLE LOAD$_k$  
defined by Eq. (25)

SINKS  
index for sinks

SOURCES  
set of pollutant-laden streams

$T_{\text{rxn}}$  
reaction temperature

TERMINAL  
set of terminal waste streams

TERMINAL LOAD$_k$  
defined by Eq. (26)

$W_i$  
flowrate of the $i$th source

$X$  
n-dimensional vector

$X^I$  
Interval

$X^I_j$  
lower bound on interval $X$

$X^U_j$  
target composition of the $j$th MSA

$X^U$  
upper bound on interval $X$

$Y$  
Interval

$Y^U_{j,k}$  
Composition of the $k$th component in the $i$th outlet stream

$\gamma^\text{max}_{j,k}$  
Maximum composition of the $k$th component in the $j$th inlet stream

$\gamma^\text{min}_{j,k}$  
Minimum composition of the $k$th component in the $j$th inlet stream

$Y^I$  
lower bound on interval $Y$

$Y^U$  
upper bound on interval $Y$

$Z_{i,k}$  
Composition of the $k$th component in the $i$th outlet stream

Greek

$\epsilon$  
Minimum allowable composition difference

$\omega_{i,k}$  
path operator for composition as defined by Eq. (9)

$\psi_i$  
Path operator for flowrate as defined by Eq. (8)

Subscripts

$I$  
index for an exiting source

$J$  
index for an entering source

$K$  
index for a targeted species

$S$  
index for a unit

Superscripts

BMI  
Before mass integration

$L$  
lower bound of an interval

SGM  
after sink/generator manipulation

$U$  
upper bound of an interval

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Appendix A. Implementation of the targets for the case study

Once the interval-based target is identified and it is decided that it is an attractive-enough target, more detailed mass integration work can be undertaken to identify cost-effective solutions that can attain the target. In this appendix, we develop the optimum solution that achieves the target for the case study.

The identified target for sink/generator manipulation was obtained by interval analysis as $W_1$, $W_2$, and $W_3$ being 0.20, 0.15, and 0.08 kg/s, respectively, with the lower bound on the TERMINAL LOAD$_k$ water being 0.43 kg/s. Now, we can use these targets to solve the path Eqs. (35)–(43) and get $T_{\text{rxn}} = 710$ K and $P_{\text{comp}} = 95$ atm. Fig. II illustrates this solution.

Next, we include recycle and interception. Since attaining the target will require the selection of a separation system, we now provide data on candidate mass separating agents MSAs. As mentioned earlier, the primary target species is water. A second species is phenol which exists at a composition of 500 ppm in the wastewater stream exiting the decanter. A process lean stream and three external MSAs are considered for removing phenol. The process lean stream is a flare gas (a gaseous stream fed to the flare) which can be used as a process stripping agent. Therefore, the seal pot can be used as a stripping column in which the flare gas strips the phenol off the wastewater while the wastewater stream constitutes a buffer solution for preventing...
back-propagation of fire. Three external MSAs are considered: a solvent extractant (S2), an adsorbent (S3), and a stripping agent (S4). The data for the candidate MSAs are given in Table I1. The equilibrium data for the transfer of the pollutant from the waste stream to the jth MSA is given by Table I1 where \( m \) is the slope of equilibrium function, \( \varepsilon \) is the minimum allowable composition difference.

Water may be recycled to two sinks; the seal pot and the water-jet compression station. The following constraints on flowrate and composition of the pollutant (phenol) should be satisfied:

**Seal pot:**
1. \( 0.10 \leq \text{flowrate of feed water (kg/s)} \leq 0.20 \)
2. \( 0 \leq \text{phenol content of feed water (ppm)} \leq 50 \)

**Makeup to water-jet compression station**
1. \( 0.18 \leq \text{flowrate of makeup water (kg/s)} \leq 0.20 \)
2. \( 0 \leq \text{phenol content of makeup water (ppm)} \leq 50 \)

Next, we represent the problem from a species viewpoint as shown in Fig. I2.

By undertaking source-sink mapping analysis (El-Halwagi & Spriggs, 1996; El-Halwagi, 1997), we identify a direct-recycle opportunity from the decanter wastewater to the seal pot (Fig. I3). Since the flare gas in the seal pot is a process MSA, the mass-pinch diagram

Fig. I1. Flowsheet after sink/generator manipulation.

Fig. I2. Problem from a species viewpoint.

Table I1
Data for the MSAs of the tire pyrolysis problem

<table>
<thead>
<tr>
<th>Stream</th>
<th>Upper bound on flowrate (kg/s)</th>
<th>Supply composition (ppmw phenol) ( x_j^s )</th>
<th>Target composition (ppmw phenol) ( x_j^t )</th>
<th>Equilibrium constant (m)</th>
<th>( \varepsilon ) ppmw phenol</th>
<th>C $ TAC$/kg MSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.15</td>
<td>200</td>
<td>900</td>
<td>0.5</td>
<td>200</td>
<td>–</td>
</tr>
<tr>
<td>S2</td>
<td>( \infty )</td>
<td>300</td>
<td>1000</td>
<td>1.0</td>
<td>100</td>
<td>0.001</td>
</tr>
<tr>
<td>S3</td>
<td>( \infty )</td>
<td>10</td>
<td>200</td>
<td>0.8</td>
<td>50</td>
<td>0.020</td>
</tr>
<tr>
<td>S4</td>
<td>( \infty )</td>
<td>20</td>
<td>600</td>
<td>0.2</td>
<td>50</td>
<td>0.040</td>
</tr>
</tbody>
</table>
can be used to evaluate extent of phenol removal in the seal pot. As shown in Fig. 14, phenol will be stripped to a composition of 200 ppm.

In order for the wastewater leaving the seal pot to be recycled to the water-jet makeup, its composition must be reduced to 50 ppm. Therefore, interception using external MSAs is required. Using the mass-pinch diagram with external MSAs (Fig. 15) and by undertaking thermo-economic analysis (El-Halwagi & Manousiouthakis, 1989a,b, 1990b,b; El-Halwagi, 1997), we deduce that the stripping agent is the optimal MSA at a total annualized cost of $65,250/year. The final solution is shown in Fig. 12. As illustrated by the foregoing analysis, it features direct recycle from the decanter to the seal pot and an intercepted recycle (using stripping) from the seal pot to the compression station.

References


