

**SYNTHESIS OF MASS EXCHANGE NETWORKS FOR BATCH PROCESS
SYSTEMS. PART 3 – TARGETING AND DESIGN FOR NETWORK WITH MASS
STORAGE SYSTEM**

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ABSTRACT

The use of mass storage system in a batch mass exchange network (MEN) enables the “reuse” of excess capacity of process mass separating agent (MSA). The mass storage is a type of mass transfer equipment employing a regenerated MSA. A regenerated MSA is firstly used to extract pollutant mass load from a rich stream at one time interval. It is then regenerated in another time interval by employing a process MSA with excess capacity to absorb its mass load. This contributes to the reduction of pollutant mass load released from process streams by utilising its excess capacity.

Techniques developed in this paper for the synthesis of a batch MEN with storage system involve the two key steps, i.e. (i) setting the minimum utility and mass storage targets ahead of network design; (ii) design a batch MEN that achieve the established targets. The utility targeting step employs the vertical cascading approach in a newly developed tool, i.e. time-dependant composition interval table (TDCIT) that has been adapted from heat exchange network synthesis (HENS) for batch processes. Prior to MEN design, the targeting procedure establishes the minimum utility (solvent) and mass storage targets for a maximum mass recovery (MMR) network. Next, the time-grid diagram (TGD) and the overall time-grid diagram (OTGD) that include the time dimension have been introduced to design a batch MEN which consists of mass storage system.

INTRODUCTION

Pinch technology was initially developed for the optimal synthesis of heat exchanger network (HEN) due to the energy crisis in the late 1970s. Since then, its application in heat exchanger network synthesis (HENS) has become well established (Linnhoff *et al.*, 1982; Gundersen and Naess, 1988). In the 1980s and mid-1990s, pinch technology has been found to have fruitful application in other energy conservation areas in process synthesis and design, to name a few, utility system design, distillation column placement, combine heat and power (co-generation) (Douglas, 1988; Smith, 1995; Shenoy, 1995).

Towards the late 1980s and early 1990s, the concept of heat recovery pinch has been applied for mass transfer processes, in particular, for the optimal synthesis of mass exchange network (MEN) (El-Halwagi and Manousiouthakis, 1989). The mass exchange network synthesis (MENS) problem can be stated as (El-Halwagi, 1997):

“Given a number N_R of waste (rich) streams and a number N_S of MSAs (lean streams), it is desired to synthesise a cost-effective network of mass exchangers that can preferentially transfer certain undesirable species from the waste streams to the MSAs. Given also are the flowrate of the each waste stream, G_i , its supply (inlet) composition x_j^s , and its target (outlet) composition y_i^t . In addition, the supply and target compositions, x_j^s and x_j^t , are given for each MSA. The flowrate of each MSA is unknown and is to be determined so as to minimise the network cost.

The candidate lean streams can be classified into N_{SP} process MSAs and N_{SE} external MSAs (where $N_{SP} + N_{SE} = N_S$). The process MSAs already exist on plant site can be used for the

removal of the undesirable species at a very low cost (virtually free). The flowrate of each process MSA that can be used for the mass exchange is bounded by its availability in the plant and may not exceed a value of L_j^c . On the other hand, the external MSAs can be purchased from the market and their flowrates are to be determined by economic considerations”.

El-Halwagi and Manousiouthakis (1989) first introduced the procedure for optimal synthesis of MEN based on the conventional heat transfer pinch analysis. They showed that by specifying the “minimum allowable composition difference, ε ” (analogous to the ΔT_{\min} in HENS), a composition pinch point could be located at the mass transfer composite curves. These mass transfer composite curves provide the minimum utility targets (minimum MSA consumption) ahead of any network design. They also established that, by following the conventional approach of PDM (Linnhoff and Hindmarsh, 1983), it is possible to obtain the maximum mass recovery network, with the minimum utility targets established.

In their later work, El-Halwagi and Manousiouthakis (1990a) presented a two-stage automated procedure for synthesising the MEN. Linear programming (LP) is used in the first stage to determine the pinch point as well as the minimum cost of MSAs while a mixed-integer linear program (MILP) is then used to minimise the number of mass exchangers in the second stage. A limitation of this procedure is that many network designs must be completed and evaluated. The procedure is therefore computationally intensive.

Papalexandri, Pistikopoulos and Floudas (1994) later developed a procedure based on mixed integer non-linear program (MINLP) to overcome the limitation of the sequential procedure in the linear programming. In this MINLP approach, they generate a network hyperstructure

which contains many networks alternatives. Optimisation is done based on this hyperstructure in order to get a minimum total annual cost (TAC). However, besides the great amount of efforts required to set up and optimise the network hyperstructure, this method does not always guarantee the generation of an optimum network (Hallale and Fraser, 1998). This is due to the fact that this hyperstructure does not take into account the thermodynamic bottleneck of the networks.

Friedler *et al.* (1996) introduced the P-graph theory to solve the MENS problems. Lee and Park (1996) later improve the technique by combining the P-graph theory with the non-linear programming (NLP). This two-step procedure determines the network structure as well as its operating conditions.

Garrard and Fraga (1998) introduce another numerical analysis technique based on genetic algorithms (GA) to solve the MEN synthesis task. This stochastic optimisation technique is based on the concept of natural evolution. MEN and MEN with regeneration are solved by this GA encoding technique proposed by Garrard and Fraga (1998).

Yet another numerical analysis technique for the MENS is the state space approach introduced by Bagajewicz, Pham, and Manousiouthakis (1998) for the design of energy efficient distillation networks (Bagajewicz and Manousiouthakis, 1992). This state space approach is then extended for multicomponent MENS by Gupta and Manousiouthakis (1994). The drawback of this approach is that there is no guarantee of a global optimal solution. Wilson and Manousiouthakis (2000) more recently presented another conceptual framework which is called the Infinite Dimensional State-space (IDEAS) approach to overcome these deficiencies.

The main drawback of the above mentioned numerical analysis approach is the difficulties in setting up and understanding the mathematical formulation. Once the mathematical program is formulated, the engineer's insight of the design process is no longer taken into account. This is essentially not favourable as in most circumstances, the engineer's decisions are also important for the design process.

Viewing the drawbacks of the mathematical formulation, Hallale and Fraser (1998) presented MENS task by handling the capital cost target based on the pinch design method. They firstly deal with the special case of MEN, the water minimisation problem, which is firstly introduced by Wang and Smith (1994). Both the utility cost and the capital cost are targeted prior to any design work. They also introduced a new graphical tool, the x - y plot to handle the capital cost targets for MENS.

A more generalised total cost targeting (utility and capital cost targeting) method for the MENS problem is later presented by the same authors (Hallale and Fraser, 2000a, 2000b, 2000c, 2000d). This "supertargeting" technique is essentially the same concept as in the HENS (Linnhoff and Ahmad, 1990). Retrofit technique for MEN has also been reported by the same authors in another publication (Fraser and Hallale, 2000a, 2000b).

The MENS concept was then extended to a much wider range of problems. These problems include the simultaneous synthesis of mass exchange and regeneration networks (El-Halwagi and Manousiouthakis, 1990b); synthesis of reactive MEN (El-Halwagi and Srinivas, 1992; Srinivas and El-Halwagi, 1994a); synthesis of combined heat and reactive MEN (Srinivas and El-Halwagi, 1994b); synthesis of waste-interception networks (El-Halwagi, Hamad and Garrison, 1996); heat induced separation networks (Dunn, Srinivas and El-Halwagi, 1995;

Dye, Berry and Ng, 1995; Richburg and El-Halwagi, 1995; El-Halwagi, Srinivas and Dunn, 1995) as well as the special case of MEN, i.e. the water minimisation problem (Wang and Smith, 1994; 1995; Dhole et al., 1996; Olesen and Polley, 1997; Sorin and Bédard, 1999; Polley and Polley, 2000; Bagajewicz, 2000; Dunn and Wenzel, 2001a, 2001b; Xiao and Seider, 2001; Hallale, 2002; Tan, Manan and Foo, 2002; Foo *et al.*, 2003).

Even though the technique for MENS has been rather established, yet, almost all of the MENS tasks have been carried out for the continuous processes. In contrast, very little work has been done on mass exchange network synthesis (MENS) for batch process systems. The batch process systems referred to in this work can be defined as processes which operate discontinuously and deliver the products in discrete amounts, with frequent starts and stops (Douglas, 1988; Smith, 1995). There is a clear need to develop a MENS procedure for batch process systems which are industrially very common as well as important.

The only paper which briefly discussed a special case of MENS, i.e. water minimisation for batch operation is reported by Wang and Smith (1995). By putting time as one of the main process variables, they attempt to maximise the driving force in each of the concentration interval so that water usage is minimised and water consumption can be targeted ahead of any network design. Since the work of Wang and Smith (1995) is limited to batch systems involving water, clearly, a more generalized procedure is needed for the synthesis of batch process systems involving MSA other than water.

The first part of this series of papers (Foo *et al.*, 2002) presented the vertical cascading method through the newly introduced *time-dependant composition interval table* (TDCIT) to identify the minimum utility targets (minimum process and external MSA consumption) for a

MEN for a batch process. We next presented two new graphical tool called the *time-grid diagram* (TGD) and *overall time-grid diagram* (OTGD) to design a minimum utility batch MEN, for system without mass storage in the second part of this series of papers (Foo *et al.*, 2003).

This paper in turn presents a two-stages approach in synthesising a batch MEN with mass storage system. In the first stage, the targeting approach employs the TDCIT to establish the network targets that include the minimum utility (solvent) and mass storage targets for a maximum mass recovery (MMR) network. In the second stage, TGD and OTGD are utilised to design a batch MEN with storage system to achieve the established targets. Two operation modes for batch process will be studied, i. e. the single batch process and repeated batch processes with storage system. The conceptual design of mass storage system is also outlined in the later part of this paper.

SYNTHESIS OF BATCH MASS EXCHANGE NETWORK

Problem statement and basic assumptions

The basic problem statements on batch MENS shall follow the problem statement on continuous MENS by El-Halwagi and Manousiouthakis (1989). However, In addition to continuous MENS problem statement, the batch MENS problem statement should include the following:

The process rich and lean streams are limited by the duration where they exist in the batch process cycle. Hence, apart from the thermodynamic limitations, integration between the process rich and lean stream is limited by the time duration where by both streams could coexist. External MSA(s) are used when process MSA is not available.

El-Halwagi and Manousiouthakis (1989) listed a few basic assumptions for the continuous MENS problem. There are:

1. The mass flowrate of each stream remains essentially unchanged as it passes through the network.
2. Within the MEN, stream recycling is not allowed.
3. In the range of composition involved, any equilibrium relation governing the distribution of a transferable component, between the i th rich stream and the j th lean stream is linear and independent of the presence of other soluble components in the rich stream.

These assumptions on the continuous MENS are also valid for the batch MENS problem.

Besides, three other key assumptions are listed as follows:

4. The mass flowrate for each stream remains essentially unchanged as it passes through the network within its respective time duration.
5. Mass transfer equilibrium between the rich and lean streams is independent of the time interval. This means that the mass transfer equilibrium and not the time duration will govern the distribution of the transferable components between the rich and lean streams, for the rich and lean streams coexisting in a given time interval.
6. Mass exchange equipment in this work is not equipped with any mass storage devices.

The fourth assumption is reasonable when the flowrate of each stream is independent of the duration when it exists. This assumption is the extension of the first assumption made by El-Halwagi and Manousiouthakis (1989) for the continuous MENS. The fifth assumption indicates that the time function will not affect the equilibrium relationship between the rich and lean streams. It also indicates that all streams have steady state properties. This is true for most mass exchange systems in industrial application. The final assumption indicates that any mass storage devices to be used are separate from the main mass exchange equipment.

Case study – coke oven gas sweetening process

To demonstrate the developed method, the basic data of an industrial case study, i.e. the coke oven gas (COG) sweetening process (El-Halwagi and Manousiouthakis, 1989a) on the continuous mode have been modified to simulate a batch system with a cycle time of 1 hour. This example has two process rich streams, i.e. COG stream (denoted by R_1) and Claus tail gas (denoted by R_2) as well as one process lean stream, which is a process MSA (aqueous ammonia, denoted by S_1). The transfer of only one component – hydrogen sulphide (H_2S) is considered. The synthesis task is to maximise the mass exchange between the process rich and lean streams, leaving the excess mass load for external MSA (in this case, a chilled methanol stream, denoted by S_2). The minimum concentration difference, ϵ is fixed at 0.0001. Rich stream R_1 exists in the process during the first 0.5 hour, while R_2 exists between 0.4 to 1.0 hour. The process MSA stream (liquid ammonia, S_1) exists from 0.3 to 0.7 hour. The synthesis task now is to get the minimum requirement of the process MSA, S_1 as well as the external MSA (i.e. the chilled methanol, S_2), for the batch process. This also involves getting the timing for the MSA usage. The MEN representation for the COG sweetening process is shown in **Figure 1**.

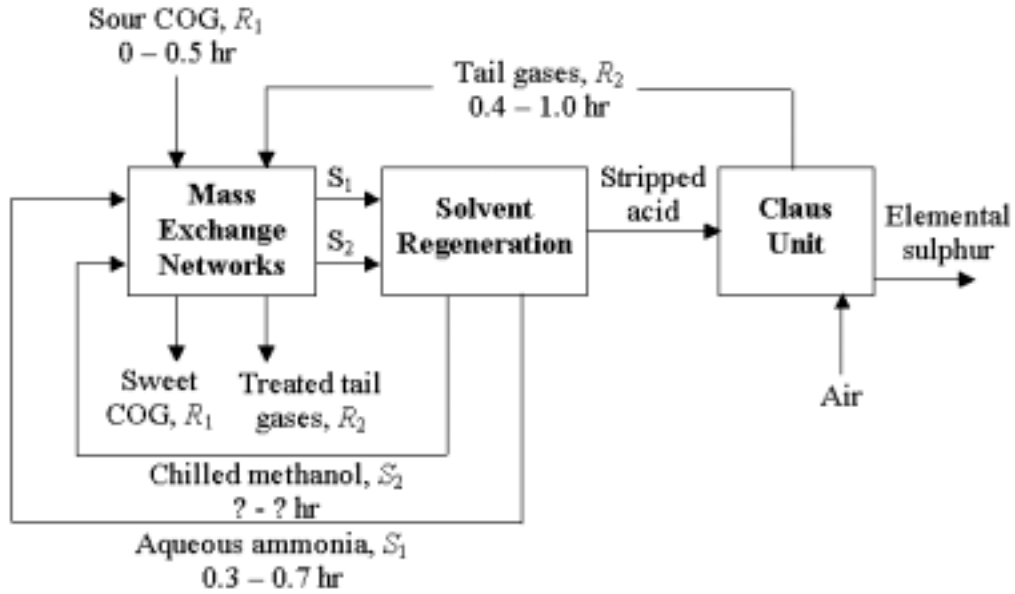


Figure 1 Batch mass exchange network representation for the COG sweetening problem

The equilibrium solubility data for H_2S in aqueous ammonia and methanol respectively is given by the following relations,

$$y = 1.45 x_1 \quad (1)$$

and

$$y = 0.26 x_2 \quad (2)$$

Data for the case study in the batch mode is shown in **Table 1**. The flowrate for each stream has been adjusted to take into account when the streams actually exist in the process. Note that the modified data in this hypothetical example have taken into account the actual operating scenario of the COG sweetening process. Time duration for any individual operation in a real COG sweetening process which varies from this case study can be easily scaled accordingly to the proposed time duration in this example.

Minimum flowrate for process MSA and external MSA are respectively given by:

$$L_1 = L_1^c - \frac{m_{H_2S,p}}{(x_1^t - x_1^s)} \quad (3)$$

and

$$L_2 = \frac{m_{H_2S,ext}}{(x_2^t - x_2^s)} \quad (4)$$

Table 1 Stream data for COG batch process

Rich stream	$G_i \times dt$ (kg)	y_i^s	y_i^t	Start	Finish	G_i (kg/hr)
				time, t^f (hr)	time, t^g (hr)	
R ₁	3240	0.0700	0.0003	0.0	0.5	6480
R ₂	360	0.0510	0.0001	0.4	1.0	600
Lean stream	$L_j^c \times dt$ (kg)	x_j^s	x_j^t	t^f (hr)	t^g (hr)	L_j^c (kg/hr)
S ₁	8280	0.0006	0.0310	0.3	0.7	20700
S ₂	∞	0.0002	0.0035		∞	∞

SINGLE BATCH PROCESS WITHOUT MASS STORAGE SYSTEM

In our previous works (Foo *et al.*, 2000, 2003), a two-stages approach is presented for MENS, for a single batch process without mass storage system. In the first stage, a newly developed tool called the *time-dependant composition interval table* (TDCIT) is introduced to target the minimum utility consumption (minimum process and external MSA) for the system (Foo *et al.*, 2000). In this approach, we maximised the reuse of the process MSA in each individual time interval. This provides us with an insight of the maximum achievable targets for mass exchange in each of the time interval, as well as the overall batch process system. **Table 2**

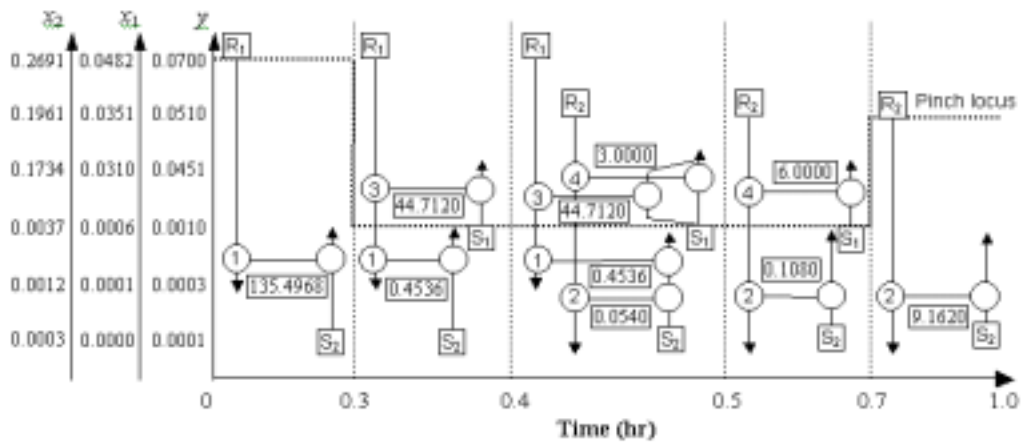
shows the TDCIT for the COG case study, operated in a single batch mode without mass storage system. Values in bold indicate the pinch location at each individual time interval.

Table 2 TDCIT for COG case study (single batch without mass storage)

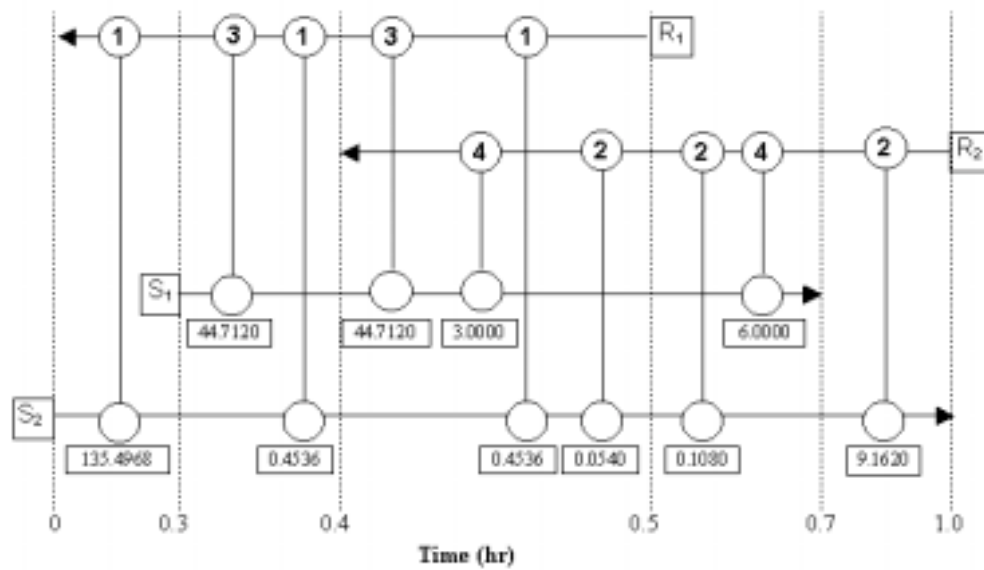
y	x ₁	Time, hr									
		0.0 – 0.3		0.3 – 0.4		0.4 – 0.5		0.5 – 0.7		0.7 – 1.0	
		Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm
0.0700	0.0482	0.0000		18.2160		15.2160		119.8560		0.0000	
		36.9360		12.3120		12.3120		0.0000		0.0000	
0.0510	0.0351	36.9360		30.5280		27.5280		119.8560		0.0000	
		11.4696		3.8232		4.1772		0.7080		1.0620	
0.0451	0.0310	48.4056		34.3512		31.7052		120.5640		1.0620	
		85.7304		-34.3512		-31.7052		-120.5640		7.9380	
0.0010	0.0006	134.1360		0.0000		0.0000		0.0000		9.0000	
		1.3608		0.4536		0.4956		0.0840		0.1260	
0.0003	0.0001	135.4968		0.4536		0.4956		0.0840		9.1260	
		0.0000		0.0000		0.0120		0.0240		0.0360	
0.0001	0.0000	135.4968		0.4536		0.5076		0.1080		9.1620	

Minimum utility targets for each time interval could be located with Eq. 3 and Eq. 4 applied in the respective time interval. For the entire process, the targeted excess capacity of H₂S removal by ammonia is 153.2880 kg/hr, while the minimum H₂S to be removed by external chilled methanol is 145.7280 kg/hr. Using Eq. 3 and Eq. 4, the mass of process MSA (L_1) and external MSA (L_2) can be calculated as 3237.6316 kg and 44160.0000 kg.

In the second stage of the synthesis task, a systematic procedure for designing a maximum mass recovery (MMR) network has been developed (Foo *et al.*, 2003). Two new graphical tools called the *time-grid diagram* (TGD) and the *overall time-grid diagram* (OTGD) that incorporate the time and composition axes have been introduced to provide a better representation of the problem during the MEN design for the batch system. These newly developed grid diagrams are shown in **Figure 2** for the COG case study, for single batch process without mass storage.



(a)



(b)

Figure 2 Network design for COG case study represented in (a) TGD ; and (b) OTGD

MENS FOR BATCH PROCESSES WITH MASS STORAGE SYSTEM

Unlike heat storage in batch heat integration, mass storage does not involve losses through mass transfer to the environment. This makes mass storage more practical to implement. Mass exchange with storage is conceptually similar to that of heat storage in batch heat integration (Kemp and Deakin, 1989a, b). The mass load rejected below a local pinch point at a given time interval can be stored and supplied above the pinch at a later time interval. This is

different from the conventional approach of pinch technology where mass or energy should not be transferred across the pinch point. Note that, for a batch process, this heuristic rules only hold within a given time interval. Mass (or heat, in heat integration) load rejected below a pinch in an earlier time interval could be supplied above the pinch of a later time interval, so long as there exist a positive driving force for mass or heat transfer. **Figure 3** illustrates the mass storage concept using the *mass transfer grand composite curve* (MTGCC). The MTGCC is adapted from the batch heat integration work by Kemp and Deakin (1989a) The MTGCC is introduced to demonstrate the usefulness of the mass storage system (**Figure 3**).

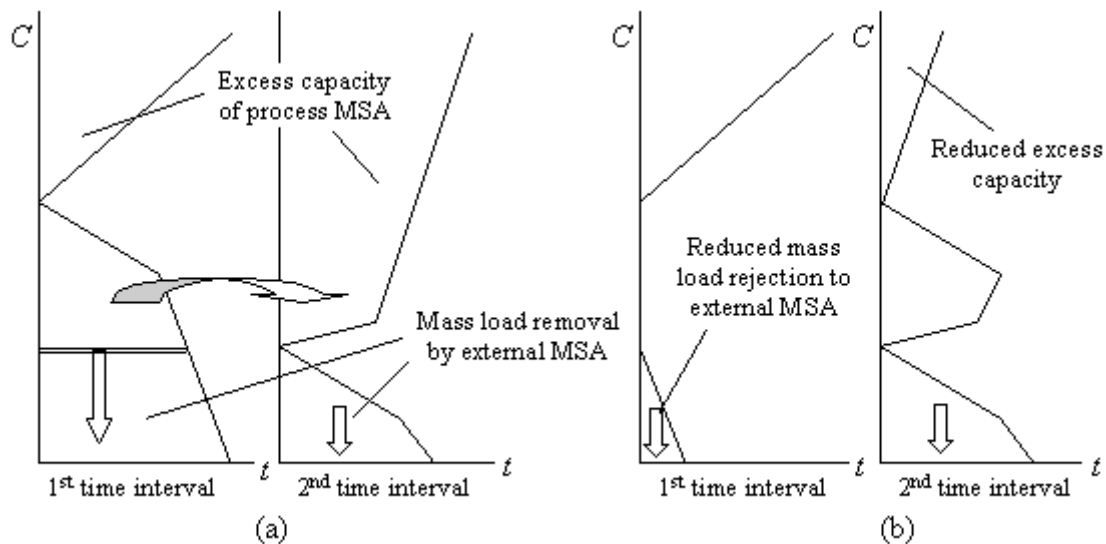


Figure 3 (a) MTGCC for individual system with MMX where no mass storage is transferred across the time interval; (b) MTGCC with storage, where a transfer of mass load is occurring across the time interval via the mass storage system

When no mass storage is installed for the MEN, mass load can only be rejected to the external MSA at the region below the pinch. Hence, excess capacity of process MSA are found above the pinch in the MTGCC (**Figure 3a**). This tends to increase operating cost of the network since more external MSA are required while the excess capacity of the process MSA are not utilised. However, with a mass storage system, mass load rejected to the external MSA at one time interval could be stored and supplied to the above pinch region at a later time interval.

This will reduce the external MSA usage and allow the excess capacity of process MSA to be utilised (**Figure 3b**). The mass storage concept can also be presented on the mass transfer composite curves, shown in **Figure 4**.

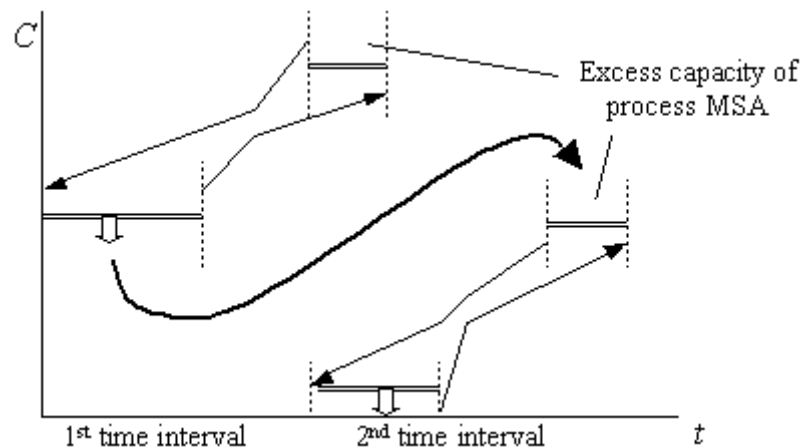


Figure 4 The same representation of mass storage in the mass transfer composite curves

Kemp and Deakin (1989a) pointed out that it is essential to obtain the storage capacity during the targeting stage. This will help during the design of a cost effective network in much reduced effort. Hence, the mass storage targeting technique will be carried out in the following sections for both single and repeated batch processes.

Targeting with mass storage within a single batch process

In order to obtain targets with storage, we have to work from one time interval to another and identify the mass load which can be stored and transferred across the time interval. **Table 2** indicates that the local pinch compositions in the time intervals between 0 – 0.3 hr and 0.7 – 1.0 hr are higher than that of the others. However, since interval 0.7 – 1.0 hr is the final time interval, only the first time interval, 0 – 0.3 hr can be used for mass storage.

Table 2 also indicates that in the time interval between 0.3 – 0.7 hr, there are negative mass loads in the composition interval between $y = 0.0010 – 0.0451$ (corresponding to $x = 0.0006 – 0.0310$). These are the sources of the excess capacity in the process MSA. Therefore, mass load stored during the first time interval (0 – 0.3 hr) will be used in these time intervals (0.3 – 0.7 hr) to eliminate the excess capacity of the process MSA.

However, to ensure a feasible mass transfer during the release of mass load between the storage and the process lean stream between time intervals 0.3 – 0.7 hr, the mass transfer driving force is to be explored. As can be seen from **Table 2**, the negative mass loads in the three time intervals start at the MSA composition level of $x = 0.0006$. Hence, mass load in the first time interval (0 – 0.3 hr) is to be stored between the maximum MSA composition of $x = 0.0482$ down to this composition level. Shown in **Table 3**, the stored mass load between these composition intervals is equivalent to 134.1360 kg. This stored mass load is then released into the system on the above pinch region between time intervals of 0.3 – 0.7 hr. This has led to an elimination of excess capacity in process MSA in the second and third time intervals (0.3 – 0.5 hr), and a reduced excess capacity in the fourth interval (0.5 – 0.7 hr) (**Table 3**).

Table 3 Time-dependant CIT for single batch process with single mass storage

y	x ₁	Time, hr									
		0 – 0.3		0.3 – 0.4		0.4 – 0.5		0.5 – 0.7		0.7 – 1.0	
		Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm
0.0700	0.0482		0.0000		0.0000		0.0000		19.1520		0.0000
		36.9360		12.3120		12.3120		0.0000		19.1520	0.0000
0.0510	0.0351	11.4696	48.4056	3.8232	16.1352	4.1772	16.4892	0.7080	19.8600	1.0620	1.0620
0.0451	0.0310	85.7304	<u>134.1360</u>	-34.3512	<u>115.9200</u>	-31.7052	<u>100.7040</u>	-120.5640	19.8600	7.9380	1.0620
0.0010	0.0006		0.0000		0.0000		0.0000		0.0000		9.0000
		1.3608		0.4536		0.4956		0.0840		0.1260	
0.0003	0.0001	0.0000	1.3608	0.0000	0.4536	0.0120	0.4956	0.0840	0.0840	0.0360	9.1260
0.0001	0.0000		1.3608		0.4536		0.5076		0.1080		9.1620

One may also store the mass load at each different composition interval in the first time interval, to be transferred to the next time interval, such as that in **Figure 4**. This option would be beneficial if there is excess capacity of the process MSA at a higher composition interval in time interval 0.3 – 0.7 hr. However, this also implies that additional mass storages are to be used at each different composition level. As in this example, the excess MSA capacity is only found in the third composition interval (i.e. at $y = 0.0010 - 0.0451$). Utilising mass storage at different composition interval in this case study is not a favourable option, since additional storage will lead to a more complex and expensive network.

Lastly, no excess capacity of process MSA is found in the final time interval (0.7 – 1.0 hr). Mass load rejected to the external MSA at the region below pinch could not be stored for further reuse since this is the final time interval in the single batch system. **Table 3** and **Table 4** also show the rearrangement of the pinch locus as a result of the storage of mass load. The mass of the process MSA (L_1) and external MSA (L_2) can be calculated as 7650.0000 kg and 3512.7273 kg.

Table 4 Time-dependant CIT for single batch process with mass storage at different composition level

y	x ₁	Time, hr									
		0 – 0.3		0.3 – 0.4		0.4 – 0.5		0.5 – 0.7		0.7 – 1.0	
		Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm
0.0700	0.0482		0.0000		0.0000		0.0000		19.1520		0.0000
		36.9360	36.9360	12.3120	36.9360	12.3120	36.9360	0.0000		0.0000	
0.0510	0.0351		0.0000		12.3120		12.3120		80.7120		0.0000
		11.4696	11.4696	3.8232	11.4696	4.1772	11.4696	0.7080		1.0620	
0.0451	0.0310		0.0000		16.1352		16.4892		100.8900		1.0620
		85.7304	85.7304	-34.3512	85.7304	-31.7052	85.7304	-120.5640		7.9380	
0.0010	0.0006		0.0000		0.0000		0.0000		0.0000		9.0000
		1.3608	0.0000	0.4536	0.0000	0.4956	0.0000	0.0840		0.1260	
0.0003	0.0001		1.3608		0.4536		0.4956	0.0840			9.1260
		0.0000		0.0000		0.0120		0.0240		0.0360	
0.0001	0.0000		1.3608		0.4536		0.5076	0.1080			9.1620

Targets with mass storage for repeated batch processes

In the industry, it is a common practice to work with repeated batches. If a repeated batch process is to be designed, the mass storage system could be useful in minimising the operational cost. In such a case, mass load from the process rich stream can be stored at the end of one process cycle to be used in the next cycle.

We noted from **Table 3** that although the pinch composition in the final time interval is at a higher level as compared to that in the second to the fourth time interval, the excess mass load rejected at this interval cannot be used in the same process cycle since this is the last time interval in a single batch process. If this process is to be designed in a repeated mode, the mass rejected below the pinch in this time interval can now be transferred to the lean stream above the pinch in the next process cycle, if the composition permits.

The DTCIT for the repeated batch operation is shown in **Table 5**. As shown in this table, the excess capacity of aqueous ammonia for the removal of H₂S for this repeated mode has been reduced to 10.1520 kg (corresponding to 10.1520 kg/hr or 0.00282 kg/s for the continuous mode of operation). Similarly, H₂S load to be removed by the external MSA has also been reduced to 2.5920 kg (corresponding to 2.5920 kg/hr or 0.00072 kg/s in continuous mode of operation). This is due to the storage of mass load of contaminant in the final time interval to be used in the later process cycle. Hence, the consumption of the external MSA (i.e. the chilled methanol) in the final time interval has also been reduced substantially due to the use of storage system. As can be seen, the utility targets in the repeated batch mode are exactly the same as in the case of a continuous process. The same situation applies in the case of heat integration for batch processes (Kemp and Deakin, 1989).

Table 5 DTCIT for repeated batch process with single mass storage

y	x ₁	Time, hr									
		0 – 0.3		0.3 – 0.4		0.4 – 0.5		0.5 – 0.7		0.7 – 1.0	
		Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm
0.0700	0.0482		0.0000		0.0000		0.0000		10.1520		0.0000
		36.9360		12.3120		12.3120		0.0000		0.0000	
0.0510	0.0351		36.9360		12.3120		12.3120		10.1520		0.0000
	0.0310	11.4696		3.8232		4.1772		0.7080		1.0620	
0.0451			48.4056		16.1352		16.4892		10.8600		1.0620
	9.0000	85.7304	143.1360		124.9200		109.7040				9.0000
0.0010	→		→	-34.3512	→	-31.7052	→	-120.5640		7.9380	→
	0.0006		0.0000		0.0000		0.0000		0.0000		0.0000
		1.3608		0.4536		0.4956		0.0840		0.1260	
0.0003	0.0001		1.3608		0.4536		0.4956		0.0840		0.1260
		0.0000		0.0000		0.0120		0.0240		0.0360	
0.0001	0.0000		1.3608		0.4536		0.5076		0.1080		0.1620

It should be noted that in repeated batch processes, the stored mass load at one time interval could actually be released to the time interval which exist before it, so long as there exist a positive mass transfer driving force (i.e. mass load is released above the pinch). This is the fact that in repeated batch processes, mass load is no longer constrained by the time variable. For example, mass load stored at time interval 0.5 – 0.7 hr during the first batch process can be fed to the time interval 0.4 – 0.5 hr in the second batch process. Hence, mass load flow in the reserve direction is possible for repeated batch processes. The TDCIT for the reverse flow of stored mass load is shown in **Table 6**. However, the reverse flow of stored mass load can only determine the overall utility targets (consumption of process and external MSAs). The targeting approach cannot determine the storage target for each individual time interval, as oppose to the case of forward stored mass load flow. This is due to the fact that the mass storage capacity is determined by the cumulative mass load fed to the storage system, in which the mass load is accumulated in time during the process operation.

Table 6 DTCIT for repeated batch process with backward flow of stored mass load

y	x ₁	Time, hr										
		0 – 0.3		0.3 – 0.4		0.4 – 0.5		0.5 – 0.7		0.7 – 1.0		
		Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	Δm	Cum. Δm	
0.0700	0.0482		0.0000		10.1520		0.0000		0.0000		0.0000	
		36.9360		12.3120		12.3120		0.0000		0.0000		
0.0510	0.0351		36.9360		22.4640		12.3120		0.0000		0.0000	
		11.4696		3.8232		26.2872		4.1772		0.7080		1.0620
0.0451	0.0310		48.4056		8.0640		16.4892		0.7080		1.0620	
		134.1360		-34.3512		-31.7052		23.2800		143.1360		134.1360
0.0010	0.0006		85.7304		0.0000		0.4956		0.0840		0.1260	
		0.0006		1.3608		0.0000		0.4956		0.0840		0.1260
0.0003	0.0001		1.3608		0.4536		0.4956		0.0840		0.1260	
		0.0000		0.0000		0.0120		0.0240		0.0360		0.1260
0.0001	0.0000		1.3608		0.4536		0.5076		0.1080		0.1620	

Network design for single batch system with mass storage

In our previous work (Foo *et al.*, 2003), only the networks with direct mass exchange within a time interval have been considered. *Indirect mass exchange*, which refers to mass being stored for use at a later time is also a possibility. The concept introduced by Kemp and Deakin (1989b) for network design of batch HEN with heat storage will be extended to the MEN design here.

The mass kept in storage system may function either as a lean or a rich stream, depending on what stream the storage mass is finally integrated with. Mass stored at any time interval will function as a lean stream if it is matched with a richer stream. On the other hand, the mass stored will function as a rich stream if it is integrated with a leaner stream.

Figure 5 shows the network design in a TGD for the case study which operates in a single batch mode with mass storage. Note that the mass load from rich stream R₁ in the first time interval in the region above the pinch, that is initially supposed to be transferred into the

external MSA can now be transferred to the mass storage system (see **Figure 2** for MEN without storage system).

By absorbing the rich stream from the first time interval, the storage system acts as a “lean stream”. Between the second and the fourth time interval the storage system acts as a “rich stream” by releasing its mass load to leaner streams which exist in these intervals. This mass storage minimises the consumption of the external MSA for the overall process.

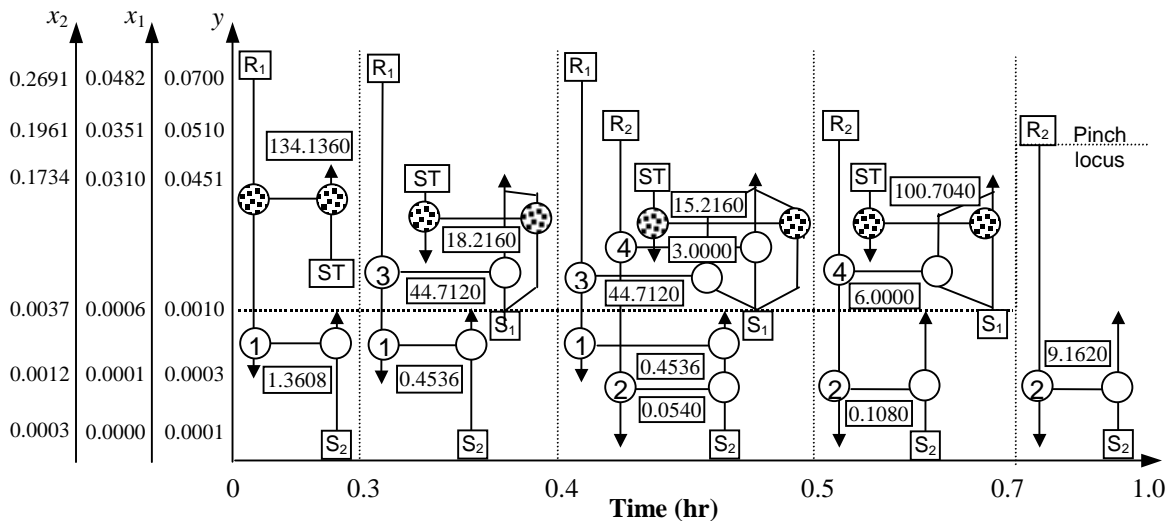


Figure 5 Network design for single batch MENS with mass storage

The use of storage system also managed to utilise the excess capacity of process MSA in the second to the fourth. Finally, it is important to note that the use of storage has resulted in a new locus of pinch composition. Recall that no change can be made for the last time interval in the case of MEN without storage since the excess capacity of the process MSA cannot be used in an earlier time interval.

A representation of the network in an OTGD is shown in **Figure 6**. A rectangular box represents the storage system. Mass load transferred to and from the storage system is

indicated by dotted arrows. The amount of mass load transferred to and from the storage system is shown in a box below the process-storage mass exchanger. The process-storage mass exchanger is represented by a cycle linked by a dotted arrow to and from the storage.

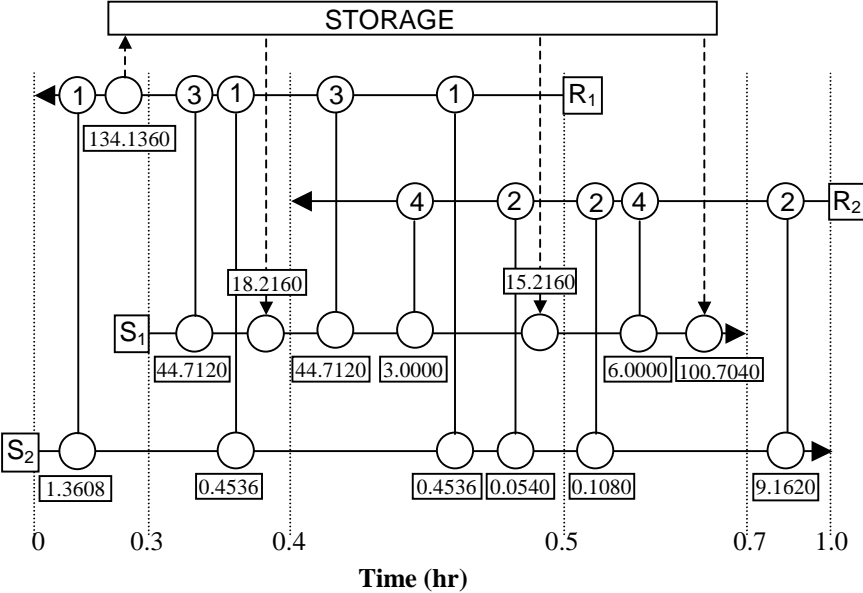


Figure 6 OTGD for a single batch process with storage

Network design for repeated batch processes with mass storage

When a batch process is operated repeatedly, the capacity in the mass storage in one process cycle can be used in a later process cycle. Kemp and Deakin (1989a, b) reported that the repeated batch system for HENS results in the same utility consumption as for the continuous system. We will demonstrate that the same concept applies for batch MENS as well.

Consider the network design for batch MENS with mass storage in **Figure 5**. Recall that the previous section, that, if we could also store the excess capacity of the process MSA available

during the final time interval, we would have been able to further minimise the consumption of the external MSA.

Figure 7 shows the network design in a TGD for the repeated batch process. A mass storage is used between the time interval of 0.7 – 1.0 hr to absorb the excess process MSA capacity. This eventually leads to the reduction of external MSA consumption and the excess capacity of process MSA in this time interval. The absorbed mass load will then be transferred to the lean stream in the later process cycle.

As shown in the time interval between 5 – 7 hr in **Figure 7**, mass load in the process-storage mass exchanger has increased with the same amount of mass load stored from the final time interval. This again has reduced the excess process MSA capacity in the fourth time interval (0.5 – 0.7 hr).

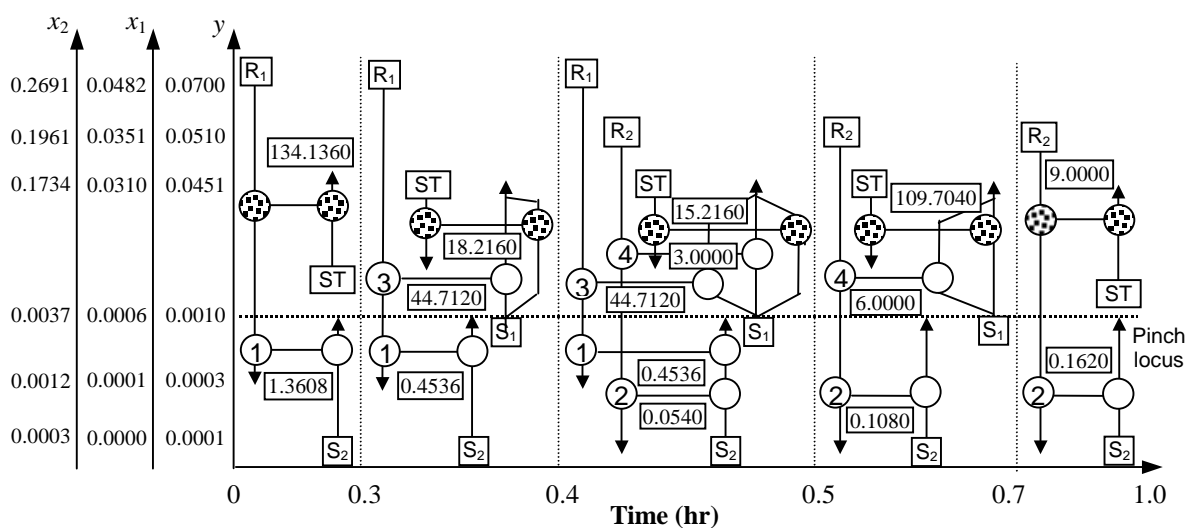


Figure 7 Network design for repeated batch MENS with mass storage

CONCEPTUAL DESIGN OF MASS STORAGE SYSTEM

Mass storage plays an important role in reducing the pollutant mass load from process streams in utilising the excess capacity of process MSA for pollution prevention purpose. In this section, the concept of mass storage system is briefly discussed. The detailed design of a mass storage system is beyond the scope of the work, thus will not be covered here.

The previous sections describe that a mass storage can function either as a lean or a rich stream, depending on which stream the stored mass is finally integrated with. The mass storage is a type of mass transfer equipment employing a regenerated MSA. The MSA is used to extract pollutant mass load from a rich stream at one time interval. The MSA from mass storage system can be regenerated by employing a process MSA with excess capacity to absorb its mass load.

The COG case study is utilised as an example to demonstrate the proposed design of a mass storage system. **Figure 7** shows a mass storage system extracting mass load from the rich streams R_1 and R_2 in the first and final time intervals respectively. The stored mass load is transferred back to the process MSA (S_1) in time interval between 0.3 to 0.7 hr. The rich streams R_1 and R_2 exist in the gas phase (sour gas stream); while the lean stream of S_1 in the liquid phase (aqueous ammonia). It is possible to utilise a solid adsorbent as the mass storage system media. The adsorbent will first extract the pollutant mass load (in this case, hydrogen sulphide) from the sour gas streams which exist in the first and final time intervals via an adsorption process. The stored mass load will be retained in the adsorbent until aqueous ammonia as the process MSA is available between the second and the fourth time intervals. In these time intervals, aqueous ammonia will be used to “leach” hydrogen sulphide from the

storage MSA. This will “regenerate” the storage MSA for further reuse. Hydrogen sulphide is then “recovered” by sending the aqueous ammonia stream to the Claus unit for sulphur recovery. Regeneration of storage MSA reduces the excess process MSA capacity and ultimately minimises the process waste.

If the process MSA used in the COG case study is in solid form (e.g. a solid adsorbent), it may be more effective to utilise a liquid solvent as a mass storage media. In this case, the storage media will first absorb pollutant mass load from the rich streams R_1 and R_2 via an absorption process. At a later time, the solvent can be regenerated by the process MSA via an adsorption process.

In the case of a liquid waste stream, three different kinds of mass storage systems could be used. If the process MSA is a liquid solvent or a solid adsorbent, one may utilise a stripping gas as the MSA for mass storage. The mass load from the rich stream is firstly absorbed by the stripping gas. For the case of liquid solvent as a process MSA, regeneration will occur by contacting the stripping gas with the process MSA at a later time to absorb the stored mass load. While in the case of solid adsorbent as a process MSA, mass storage media regeneration is done via the adsorption process. When the process MSA is a gaseous stream, a liquid solvent can be used as a mass storage media. Through solvent extraction and stripping, the pollutant mass load can be transferred to the storage system at a given time and released back to the process at a later time interval.

From the above example, we have seen that the selection of mass transfer operation for mass storage system is dependant upon the phase of the rich streams as well as the process MSA. **Table 7** summarises some typical kinds of mass transfer operations associated with mass storage system for the different combinations of waste streams and process MSA.

Table 7 Mass storage system media selection

Rich phase	Lean phase	Mass transfer operation involved	Proposed MSA media
Gas	Liquid	Adsorption / leaching	Solid adsorbent
Gas	Solid	Absorption / adsorption	Liquid solvent
Liquid	Liquid	Stripping / absorption	Stripping gas
Liquid	Solid	Stripping / adsorption	Stripping gas
Liquid	Gas	Extraction / stripping	Liquid solvent

CONCLUSION

A systematic procedure for synthesising a minimum utility batch MEN with mass storage system has been developed. In the first stage, the utility targeting step employs the vertical cascading approach in a newly developed tool, i.e. time-dependant composition interval table (TDCIT) to establish the minimum utility (solvent) and mass storage targets for a maximum mass recovery (MMR) network. The two cases studied, i.e. single and repeated batch processes with storage system have proven that the established targets for the indirect (via mass storage) mass exchange can be achieved through a systematic network design methodology developed utilising the two new graphical tools called the time-grid diagram (TGD) and the overall time-grid diagram (OTGD). The conceptual design of the mass storage system is also briefly outlined in this paper. It is shown that the selection of mass transfer operation for the use of a mass storage system is dependent upon the phase of the rich streams and the process MSA.

NOMENCLATURE

G_i	mass of rich stream i , kg
L_j	mass of lean stream j , kg
m_j	slope of equilibrium line of component (contaminant) in lean stream j
N	number of streams
R	set of rich streams
S	set of lean streams
T	temperature
x	composition in lean stream (mass/mole fraction)
y	composition in rich stream (mass/mole fraction)

Greek letter

ε	minimum composition difference
Δ	difference

Subscripts

H_2S	hydrogen sulphide removed by process or external MSA
i	rich stream number
j	lean stream number
R	set of rich streams
S	set of lean streams
SP	process MSA
SE	external MSA

Superscript

c	constraint value
f	starting time
g	ending time
s	supply value
t	required target value

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