

Separation system synthesis of fractional crystallization processes with heat integration

Luis A. Cisternas^{a,*}, Carmen P. Guerrero^a, Ross E. Swaney^b

^a Department of Chemical Engineering, Universidad de Antofagasta, Casilla 170, Antofagasta, Chile

^b Department of Chemical Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA

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Abstract

A methodology is presented for the synthesis of fractional crystallization processes with heat integration. The methodology is based on the construction of three networks. The first network is based on the identification of feasible thermodynamic states. Using equilibrium data for a candidate set of potential operation point temperatures, a network flow model is constructed to represent the set of potential separation flowsheet structures that can result. In this network the nodes correspond to multiple saturation points, solute intermediate, process feeds and end products. The second network is used to represent the variety of tasks that can be performed at each multiple saturation point. Multiple saturation nodes can be used for different tasks depending on the characteristic of the input and output streams. These tasks include cooling crystallization, evaporative crystallization, reactive crystallization, dissolution, and leaching. This multiple task condition for each equilibrium state is modelled using disjunctive programming and then converted into a mixed integer program. Heat integration is included using a heat exchanger network which can be regarded as a transshipment problem. The method is illustrated through the design of two salt separation examples. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fractional crystallization; Heat integration; Process design; Salt separation

1. Introduction

Fractional crystallization is a separation technique employed to produce a wide variety of materials, including production of potassium chloride, potassium sulphate, sodium sulphate, potassium nitrate, boric acid, etc. The technique consists of sequences of heating, cooling, evaporation, dilution, solventing-out, salting-out, and solid–liquid separation. In the last seven years several articles have been published on the synthesis of crystallization-based separation. There are two major approaches for the design of the flowsheet configuration and its operating conditions. In one approach, the phase equilibrium diagram is used for the identification of separation schemes (Cisternas & Rudd, 1993; Berry & Ng, 1996; Berry, Dye, & Ng, 1997). This procedure can be mixed with heuristic rules to determine the flowsheet. While this procedure is easy to

understand, it is relatively simple to implement only for simple cases. For more complex systems, such as multi-component systems, multiple temperature operation, or systems that form double salts, the procedure is very difficult to implement because the graphical representation is complex and because there are many alternatives to study. The second strategy is based on simultaneous optimization using mathematical programming based on a network flow model between feasible thermodynamic states (Cisternas & Swaney, 1998; Cisternas, 1999).

Although in terms of energy requirements crystallization requires much less energy for separation than does distillation or other commonly used methods of purification, energy cost can have an impact on process economics and process design (Rajagopal, Ng, & Douglas, 1988). However, does not appear to be a literature on process synthesis of these systems with heat integration. In this work a methodology is presented for the synthesis of fractional crystallization separation schemes with heat integration.

* Corresponding author.

E-mail address: lcisternas@uantof.cl (L.A. Cisternas).

2. Model development

2.1. Networks for fractional crystallization with heat integration

The model proposed in this paper is composed of three major networks that will be described in this section. These networks are: (1) the thermodynamic state network; (2) the task network; and (3) the heat integration network. Based on these networks a mathematical model will be generated to solve the process synthesis problem.

The first network is based on the identification of feasible thermodynamic states. Using equilibrium data for a candidate set of potential operating point temperatures, a thermodynamic state network flow model is constructed to represent the set of potential separation flowsheet structures that can result. This representation was introduced by Cisternas and Swaney (1998) for two solute systems and by Cisternas (1999) for multicomponent systems. The crystallization, dissolution, leaching, evaporation, and dilution steps can be represented in terms of material flows between particular thermodynamic equilibrium states. Therefore, knowing the phase, compositions, and temperatures pertaining to each state, a network model can be constructed. Fig. 1 shows the thermodynamic state network representation for a two solute system at two temperatures. The system forms an intermediate product (double salt) at one temperature. The structure involves feeds, multiple saturation points, intermediate product, and end products. It is possible to assume that operation states are equilibrium states because in most cases the process of crystallization is slow and the final mother liquor is in contact with a sufficiently large crystal surface. Therefore, mother liquor concentration is substantially that

of a saturated solution at the final temperature in the process. Readers unfamiliar with the thermodynamic state network representation are referred to Cisternas (1999) for additional details.

The second network is the task network. Each multiple saturation state can be used for different task depending on the characteristics of the input and output stream. For example, if solvent is added to an equilibrium state the task can be: (1) a leaching step if the feed is solid; (2) a cooling crystallization step if the feed is a solution with a higher temperature; or (3) a reactive crystallization step if the feed is a crystalline material that decomposes at this temperature or in the solution fed to this state (examples are the decomposition of schonite to form potassium sulphate, the decomposition of carnallite to form potassium chloride, or the conversion of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ to Na_2SO_4). In the same way, if solvent is removed from an equilibrium state the task can be: (1) a cooling crystallization (vacuum crystallization) if the feed fed is at a higher temperature; (2) an evaporative crystallization step; or (3) a reactive crystallization step. Fig. 2 shows a task network that includes leaching, cooling crystallization, and evaporative crystallization.

After the tasks are identified, it is necessary to determine what type of equipment can perform each task. In this work a single equipment unit is assigned at each task. Several alternatives exist for leaching, which include in situ leaching, vat leaching, agitation leaching, etc. (Prabhudesai, 1988). Potential crystallizers can be chosen that meet the requirements for: (a) product size; (b) product quality; and (c) scale of operations (Bennett, 1993).

The third network, a heat exchange network, can be regarded as a transshipment problem as in Papoulias and Grossmann (1983). This transshipment problem can

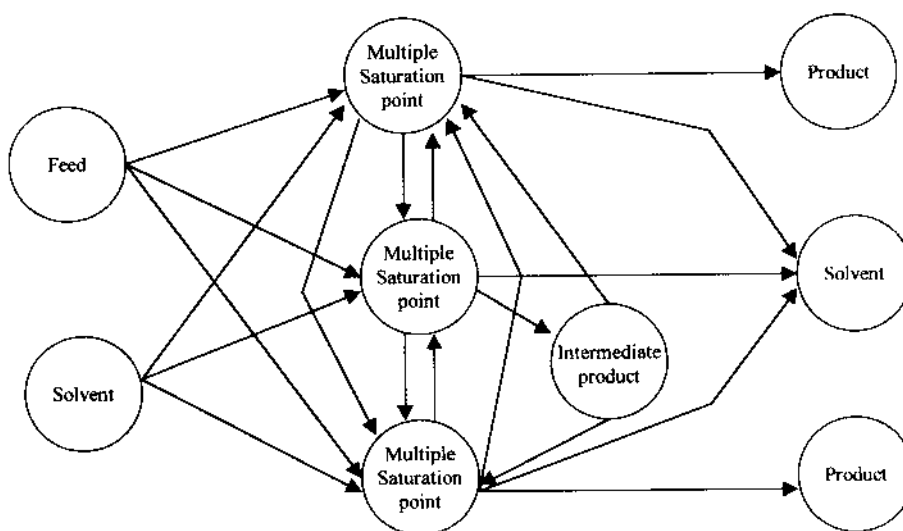


Fig. 1. Example of thermodynamic state network.

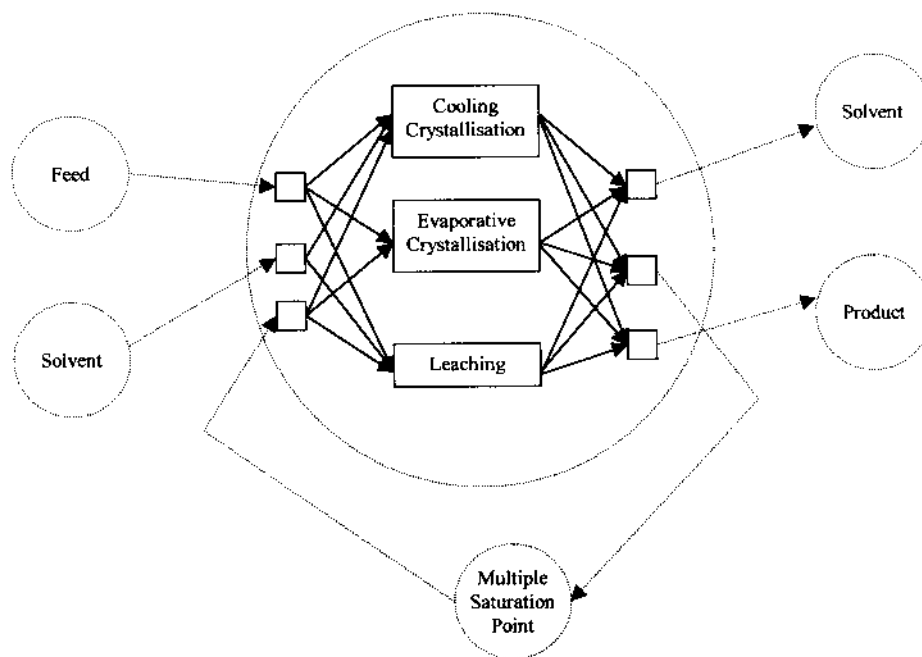


Fig. 2. Task network.

be formulated as a linear programming problem. In this representation hot streams (source nodes) and cold streams (destination nodes) corresponds to the arcs in the thermodynamic state network. Consequently, the heat integration model does not include the crystallizer heat duties. Readers unfamiliar with heat integration via the transshipment representation are referred to Papoulias and Grossmann (1983) for additional details.

2.2. Mathematical formulation

Having derived the networks for the separation problem, a mathematical programming formulation is presented for each network to select the optimum flowsheet alternative of the separation sequence.

2.3. The thermodynamic state network

The mathematical formulation for this network is the same developed by Cisternas (1999) which gives a LP problem if coprecipitation is not allowed and NLP problem if coprecipitation is an alternative. Here the LP version is described. More detail can be found in Cisternas (1999). First, the set of thermodynamic state nodes will be defined as:

$$s = \{s, \text{all nodes in the system}\}$$

This includes feeds, products, multiple saturation points or operation points, and intermediate solute products. The components, solutes and solvents, will be denoted by the set $I = \{i\}$. The arcs, which denote streams between nodes, will be denoted by $L = \{l\}$.

The following subsets are defined:

$$S_F = \{s | s \in S, \text{ feed nodes with flow rates of species } i \in I \text{ specified}\}$$

$$S_P = \{s | s \in S, \text{ product nodes with flow rates of species } i \in I \text{ specified}\}$$

$$S_M = \{s | s \in S, \text{ multiple saturation nodes and intermediate solute products}\}$$

$$S^{\text{in}}(s) = \{l | l \in L, \text{ is an inlet to node } s, s \in S_M\}$$

$$S^{\text{out}}(s) = \{l | l \in L, \text{ is an outlet from node } s, s \in S_M\}$$

$$F(s) = \{l | l \in L, \text{ is an outlet from node } s, s \in S_F\}$$

$$P(s) = \{l | l \in L, \text{ is an inlet to node } s, s \in S_P\}$$

$$I_P(s) = \{i | i \in I, \text{ is a component specified in node } s, s \in S_P\}$$

$$I_F(s) = \{i | i \in I, \text{ is a component specified in node } s, s \in S_F\}$$

Each stream l is associated with the variable mass flow rate w_l and with the parameters $x_{l,i}$, the composition of component i of stream l .

Having defined the sets, parameters, and variables that describe the overall network for the separation problem, the constraints that apply are as follows:

2.3.1. Mass balance for each component in operation point nodes

$$\sum_{l \in S^{\text{in}}(s)} w_l \cdot x_{l,i} - \sum_{l \in S^{\text{out}}(s)} w_l \cdot x_{l,i} = 0, \quad s \in S_M, i \in I \quad (1)$$

2.3.2. Specification for feeds flow rates

$$\sum_{i \in F(s)} w_i x_{i,j} = C_{s,j}^F, \quad s \in S_F, i \in I_F(s), \quad (2)$$

where $C_{s,j}^F$ is the desired flow rates of species i in feed s .

2.3.3. Specification for product flow rates

$$\sum_{i \in P(s)} w_i x_{i,j} = C_{s,j}^P, \quad s \in S_P, i \in I_P(s) \quad (3)$$

where $C_{s,j}^P$ is the desired quantity of component i in the final product s .

2.4. The heat integration network

In order to consider heat integration, the approach followed by Papoulias and Grossmann (1983) will be used in this work. We consider the case without constrained matches for simplicity in this work, but constrained matches can be easily included. First, it is considered that there is a set $K = \{k\}$ of temperature intervals that are based on the inlet temperatures of the process streams, highest and lowest stream temperatures, and of the intermediate utilities whose inlet temperatures fall within the range of temperatures of the process streams. The following index sets are defined:

- $H_k = \{l | l \in L, \text{ hot stream that supplies heat to interval } k \in K\}$
- $C_k = \{l | l \in L, \text{ cold stream that demands heat from interval } k \in K\}$
- $V_k = \{m | \text{hot utility that supplies heat to interval } k \in K\}$
- $W_k = \{n | \text{cold utility that demands heat from interval } k \in K\}$

Fig. 3 considers a given temperature interval k , where Q_m^V , Q_n^W and R_k are nonnegative variables that represent the heat load of hot utility m , heat load of cold utility n , and heat residual exiting interval k , respectively. $(C_p \Delta T)_{lk}^H$ and $(C_p \Delta T)_{lk}^C$ are known parameters that represent the heat content per unit mass of hot stream $l \in H_k$ and cold stream $l \in C_k$ in interval k . The only constraints that apply are heat balances around each temperature interval k :

$$R_k - R_{k-1} - \sum_{m \in V_k} Q_m^V + \sum_{n \in W_k} Q_n^W = \sum_{l \in H_k} w_l (C_p \Delta T)_{lk}^H - \sum_{l \in C_k} w_l (C_p \Delta T)_{lk}^C, \quad k \in K \quad (4)$$

where the heat residuals entering the first interval and exiting the last interval are equal to zero.

2.5. The task network

A task network is constructed for each multiple saturation point node $s \in S_M$. Let $T(s) = \{t\}$ define the set of conditional tasks in the multiple saturation point node $s \in S_M$. This network requires the use of discrete variables, y_t , to represent the choices of task t within each node $s \in S_M$, with which the model becomes a mixed integer linear program. The following subsets are defined:

- $S_d^{out}(s) = \{l | l \in L, \text{ the solid outlet from nodes, } s \in S_M\}$
- $S_s^{out}(s) = \{l | l \in L, \text{ the solvent outlet from nodes, } s \in S_M\}$

The variables are defined as follows: G_{it}^m are the internal mass flow rates from stream l to task t , G_{it}^{out} are the internal mass flow rates from task t to stream l , Q_{ts}^C are the heat loads of crystallization or dissolution in each task t , Q_{ts}^S are the heat loads of evaporation in each task t , VC_{ts} and FC_{ts} are the variable and fixed costs incurred for the equipment associated with the task t . The parameters are defined as follows: HQ_{ts} is the crystallization/dissolution heat per unit mass product in

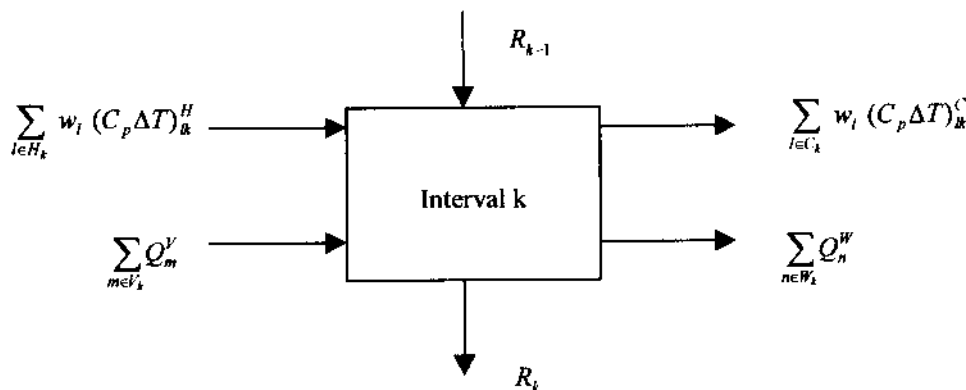


Fig. 3. Temperature interval k for the heat integration network.

each task t of node $s \in S_M$, HS_{ts} is the latent heat of evaporation in task t of node $s \in S_M$, α_{ts} and β_{ts} are the fixed and variable cost coefficients of task t of node $s \in S_M$.

With compounds whose solubility increases with increasing temperature, there is usually an absorption of heat when the compound dissolves, which is called the heat of solution. In compounds with decreasing solubility, as the temperature increases, there is an evolution of heat when solution occurs. When there is no change in solubility with temperature, there is no heat effect. Heats of solution are generally reported as the change in enthalpy associated with the dissolution of a quantity of solute in an excess of pure solvent.

At equilibrium the heat of crystallization is equal and opposite in sign to the heat of solution. Using the heat of solution at infinite dilution as equal but opposite in sign to the heat of crystallization is the equivalent, however, of neglecting the heat of dilution. With many chemicals the heat of dilution is small in comparison with the heat of crystallization and the approximation is acceptable.

The formulation, using disjunctive programming (a set of constraints of which at least one must be valid), is given by:

$$w_i = \sum_{l \in T(s)} G_{il}^{in}, \quad l \in S^{in}(s), s \in S_M$$

$$w_i = \sum_{l \in T(s)} G_{il}^{out}, \quad l \in S^{out}(s), s \in S_M$$

$$\sum_{l \in S^{in}(s)} G_{il}^{in} = \sum_{l \in S^{out}(s)} G_{il}^{out}, \quad l \in T(s), s \in S_M$$

$$\left[\begin{array}{l} y_{ts} \\ FC_{ts} = \alpha_{ts} \\ VC_{ts} = \beta_{ts} \sum_{l \in S^{in}(s)} G_{il}^{in} \\ Q_{ts}^C = HQ_{ts} G_{il}^{out}, l \in S^{out}(s) \\ Q_{ts}^S = HS_{ts} G_{il}^{out}, l \in S^{out}(s) \end{array} \right] \vee \left[\begin{array}{l} \neg y_{ts} \\ FC_{ts} = 0 \\ VC_{ts} = 0 \\ Q_{ts}^C = 0 \\ Q_{ts}^S = 0 \end{array} \right], t \in T(s), s$$

$$s \in S_M(s) \tag{5}$$

$$g(y_{ts}) = \text{True}$$

$g(y_{ts})$ represents the logic relations between Boolean variables to select the task based on input/output streams properties (Raman & Grossmann, 1991). The model of Eq. (5) is transformed into a MILP form (Turkay & Grossmann, 1996).

2.6. The objective function

The objective function is to minimise the venture cost. The following equation can be used as an objective function.

$$\min \sum_{s \in S_M} \sum_{t \in T(s)} (FC_{ts} + VC_{ts} + c_{ts}^C Q_{ts}^C + c_{ts}^S Q_{ts}^S) + \sum_{m \in U} c_m Q_m^V + \sum_{n \in W} c_n Q_n^W \tag{6}$$

Eq. (6) represents the total cost given by the investment and utility cost. In this way, the objective function in Eq. (6), subject to constraints in Eqs. (1)–(5) defines a mixed integer linear programming problem. The variables to be optimised are mass flow rates, w_i ; heat load of hot utility m , Q_m^V ; heat load of cold utility n , Q_n^W ; heat residual exiting interval k , R_k ; the internal mass flow rates from stream l to task t , G_{il}^{in} ; the internal mass flow rates from task t to stream l , G_{il}^{out} ; heat loads of crystallization or dissolution in each task t , Q_{ts}^C ; the heat loads of evaporation in each task t , Q_{ts}^S ; variable and fixed cost, VC_{ts} and FC_{ts} ; and the binary variables, y_{ts} . The numerical solution to the MILP problem can be obtained with standard algorithms.

2.7. Limitation of this work

The size, shape, and size distribution of particles in a particulate product are important for several reasons. For example, particles with very small mean size product are difficult to centrifuge, wash, and package. The kind and level of impurities in the solid product are influenced by the method of separation. For example, leaching produces solid with a high level of impurities if compared to crystallization. Therefore, it is important to include solid processing operation such as centrifugation, washing and drying. These operations are not included in this model, but further development is underway.

3. Illustrative examples

Two examples will be used to illustrate the method. The first example consists of the separation of potassium chloride from sylvinit, a mixture of potassium chloride and sodium chloride. The production of potassium chloride and magnesium chloride from the double salt carnallite is used as second example.

3.1. Potassium chloride production

This example considers the production of potassium chloride from 100 000 ton/year of sylvinit (47% KCl, 52.3% NaCl). Data are given in Table 1. The thermodynamic state network is the same used in example 1 in Cisternas (1999). The task network includes leaching, cooling crystallization, and evaporative crystallization. The solution found is shown in Fig. 4. The optimal solution divides the feed into two parts. This is the same solution found by Cisternas and Swaney (1998),

Table 1
Data for example 1

Feed rate (sylvinites)	100 000 tons/year
Solubilities	
KCl weight percent at multiple saturation points	11.7% at 20°C; 22.2% at 100°C
NaCl weight percent at multiple saturation points	20.25% at 20°C; 15.90% at 100°C
Heat capacities	
Water	1.00 Mcal/(ton °C)
Hot streams	0.84 Mcal/(ton °C)
Cold streams	0.81 Mcal/(ton °C)
Latent heat of vaporization	
	586,602 Mcal/ton at 20°C
	539,421 Mcal/ton at 100°C
Crystallization dissolution heat	
KCl	+ 59,114 Mcal/ton
NaCl	+ 19,897 Mcal/ton
Fixed cost coefficients, α_i	
Cooling crystallization	20 000 \$/year
Evaporative crystallization	27 636 \$/year
Leaching	681 \$/year
Variable cost coefficients, β_i	
Cooling crystallization	0.2200 \$/ton/year
Evaporative crystallization	0.5570 \$/ton/year
Leaching	0.0229 \$/ton/year
Utility cost	
Steam	0.0102 \$/Mcal
Cooling water	0.0018 \$/Mcal

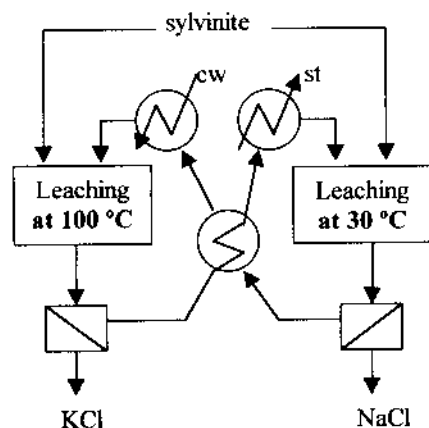


Fig. 4. Solution for example 3.1.

Cisternas (1999), where both NaCl and KCl are obtained by leaching. However, the solution obtained in this work includes task selection and heat integration. The KCl produced can have insoluble impurities because it is obtained by leaching. Therefore, further solid operation, for example recrystallization, may be needed. If the cost parameters of KCl leaching increase because

of these solid operations, the model will select cooling crystallization to produce KCl.

3.2. Salts production from Carnallite

The problem consists of separating potassium chloride and magnesium chloride from 100 000 ton/year of the double salt carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Equilibrium data from Linke and Seidell (1965) are shown in Table 2. Thermal properties and cost data are given in Table 3.

The thermodynamic state network, Fig. 5, can be constructed using the relative composition as described by Cisternas (1999). The open arrows in Fig. 5 represent the numerous feasible interconnecting paths that have been omitted for clarity. These numerous feasible interconnecting path can be represented by using the

Table 2
Equilibrium data for example 2

Key	Temperature (°C)	Saturated solution (wt%)		Solid phase
		KCl	MgCl ₂	
C1	35	3.80	27.32	KCl + carnallite
C2	35	0.14	36.17	MgCl ₂ · 6H ₂ O + carnallite
H1	105	7.00	30.82	KCl + carnallite
H2	105	1.07	40.75	MgCl ₂ · 6H ₂ O + carnallite

Table 3
Data for example 2

Feed rate carnallite	1×10^6 tons/year
Heat capacities	
Water	1.00 Mcal/(ton °C)
Hot streams	0.84 Mcal/(ton °C)
Cool streams	0.81 Mcal/(ton °C)
Temp./latent heat of vaporization for water	
	35°C 578,165 Mcal/ton
	105°C 536,099 Mcal/ton
Crystallization dissolution heat (+/-)	
KCl	59,114 Mcal/ton
MgCl ₂ · 6H ₂ O	- 35,675 Mcal/ton
Carnallite	55,807 Mcal/ton
Fixed cost coefficients, α_i	
Cooling crystallization step	11 200 \$/year
Evaporative crystallization step	4800 \$/year
Reactive crystallization step	33 066 \$/year
Variable cost coefficients, β_i	
Cooling crystallization step	0.205 \$/ton/year
Evaporative crystallization step	0.9205 \$/ton/year
Reactive crystallization step	0.584 \$/ton/year
Steam cost	0.0102 \$/Mcal
Cooling water cost	0.0018 \$/Mcal

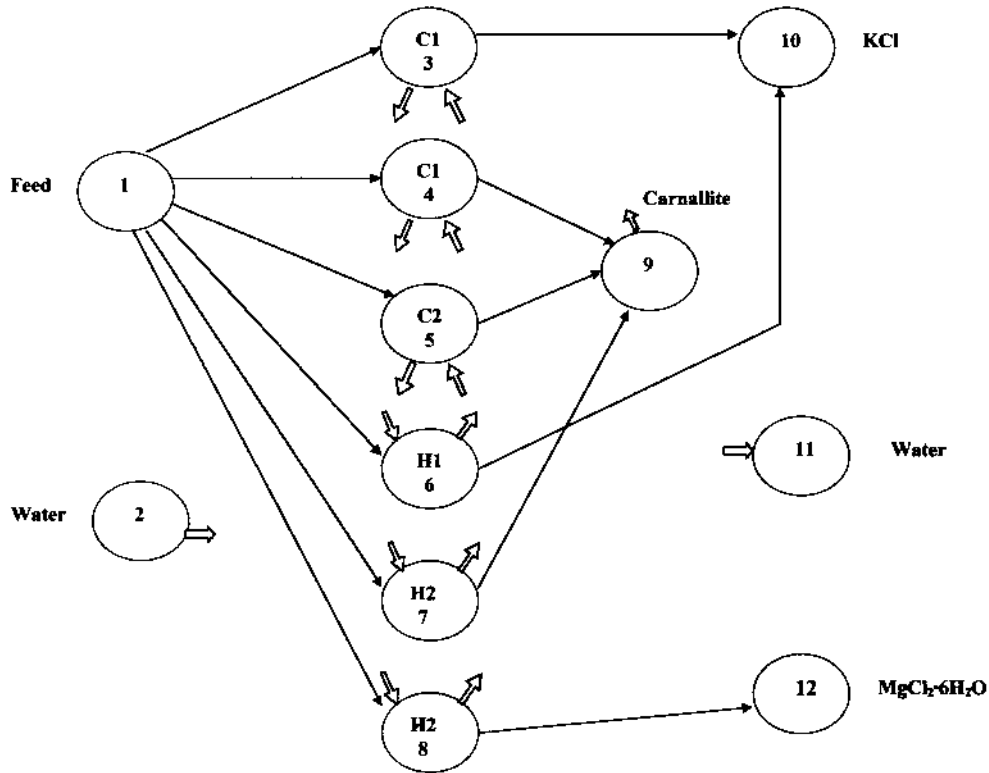


Fig. 5. Thermodynamic state network for example 3.2.

Table 4
Connectivity matrix for the thermodynamic state network of Fig. 5

Node		3	4	5	6	7	8	9	10	11	12
		C1	C1	C2	H1	H2	H2	DS	KCl	Water	MgCl ₂
1	Feed	1	1	1	1	1	1	0	0	0	0
2	Water	1	1	1	1	1	1	0	0	0	0
3	C1	0	0	1	0	1	0	0	1	1	0
4	C1	0	0	1	0	1	0	1	0	1	0
5	C2	0	0	0	0	0	1	1	0	1	0
6	H1	1	1	1	0	1	0	0	1	1	0
7	H2	0	0	1	0	0	0	1	0	1	0
8	H2	0	0	1	0	0	0	0	0	1	1
9	DS ^a	1	0	0	1	0	0	0	0	0	0

^a DS, Carnallite.

connectivity matrix. Each element represents an arc in the network and is described by the following

$A_{i,j} = 1$, if there is an arc from node i to node j ;

and

$A_{i,j} = 0$, if there is not an arc from node i to node j .

Table 4 is the connectivity matrix for this example. From this matrix it is easy to construct the $S^{in}(s)$ and $S^{out}(s)$ sets. The task network includes reactive crystallization, cooling crystallization and evaporative crystal-

lization. The heat integration network has three temperature intervals.

The solution found is shown in Fig. 6. The heat transfer units have been selected using the MILP transshipment model as described by Papoulias and Grossmann (1983).

4. Conclusions

The objective of this paper has been to present a method for determining the desired process flowsheet

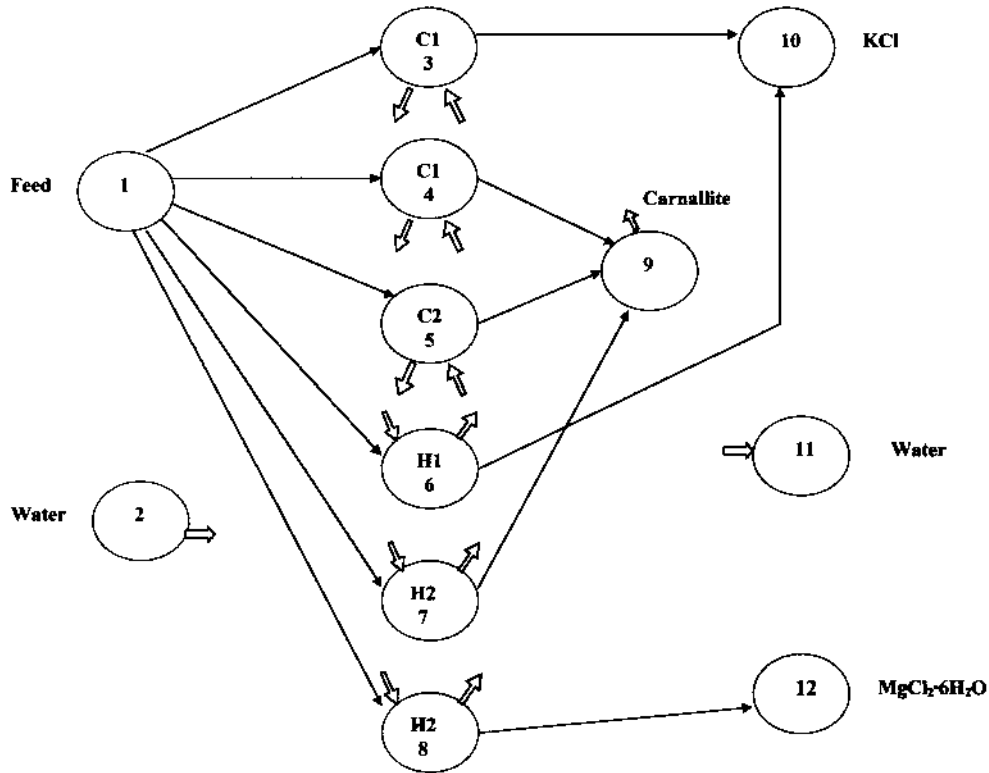


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2	Water	1	1	1	1	1	1	0	0	0	0
3	C1	0	0	1	0	1	0	0	1	1	0
4	C1	0	0	1	0	1	0	1	0	1	0
5	C2	0	0	0	0	0	1	1	0	1	0
6	H1	1	1	1	0	1	0	0	1	1	0
7	H2	0	0	1	0	0	0	1	0	1	0
8	H2	0	0	1	0	0	0	0	0	1	1
9	DS ^a	1	0	0	1	0	0	0	0	0	0

^a DS, Carnallite.

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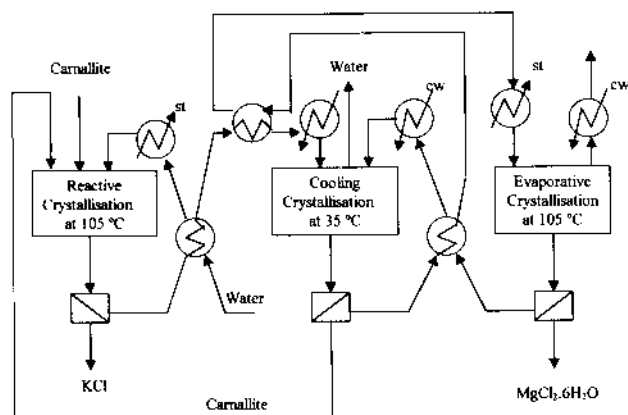


Fig. 6. Solution for example 3.2.

for fractional crystallization processes. To achieve this goal, a systematic model was introduced consisting of three networks; the thermodynamic state network, the heat integration network, and the task network. Once the representation is specified, the problem is modelled as a MILP problem. Examples were included to illustrate the method.

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