



Flowsheet synthesis of fractional crystallization processes with cake washing

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Abstract

A flowsheet synthesis methodology is presented for the design of fractional crystallization processes. The methodology is based on four interconnected/nested networks. The first network is derived by identifying a set of thermodynamic states providing a basis for feasible separation alternatives. In this network, the nodes correspond to multiple saturation points, solute intermediates, and process feeds and end products. The second network type represents the variety of tasks that can be performed at each multiple saturation point. These tasks include cooling crystallization, evaporative crystallization, reactive crystallization, dissolution, and leaching. Heat integration is incorporated using the transshipment formulation to represent the heat exchanger network. The fourth network represents the filtration and cake washing alternatives. The cake wash and task networks are modeled using disjunctive programming and then converted into a mixed-integer program. The method is applied to the design of three salt separation example problems. The optimal design costs are seen to depend on design parameters such as product impurity level and liquid retention in the cake. The advantage of an integrated synthesis approach is demonstrated.

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1. Introduction

The synthesis of fractional crystallization processes involves the selection of the flow configuration, operating conditions, and equipment. Synthesis methods for these systems typically follow one of two approaches. In the first type, constructions in the phase equilibrium diagram are used to identify separation schemes (for example Berry, Dye, & Ng, 1997; Cisternas & Rudd, 1993; Dudczak, 1996). While easy to understand, these methods are simple to implement only for simple cases. For the more complex systems that arise, e.g. with several-product systems and multiple operation temperatures, such procedures are difficult to implement because the graphical representation is complex and frequently higher-dimensional, and because there are many alternatives to evaluate. The second type of approach applies mathematical programming to optimize a network flow model constructed between feasible thermodynamic states (Cisternas, 1999; Cisternas & Swaney, 1998; Cisternas, Guerrero, & Swaney, 2001; Cisternas, Torres, Godoy, & Swaney, 2003).

In crystallization and leaching operations, filtration, washing, and drying are important issues that can impact both product quality and process economics. For example, usually filter or centrifuge cake must be washed to remove residual mother liquor, either to remove liquid impurities from a valuable solid product, or to increase the recovery of a liquid product from the cake. These issues have been discussed by Chang and Ng (1998), who utilized heuristics for design purposes.

The objective of this work is to address the cake washing issue using mathematical programming, extending our preceding method for synthesis of fractional crystallization processes. Drying is not treated explicitly here because dryers normally operate without recycle streams, and thus can be designed sequentially afterward, independently of the design of the other process components.

2. Model development and formulation

The synthesis model consists of simultaneously solving a set of coupled component networks of four types: (1) the thermodynamic state network, (2) the corresponding task networks, (3) the heat integration network, and (4) the cake

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Nomenclature

Sets

$E(Lw)$	washing/reslurry stages e for the solid stream products $l \in Lw$
$H_k, C_k, V_k,$ and U_k	hot streams, cold streams, hot utilities, cold utilities in temperature interval k
I	all components i (solutes and solvents)
$I_F(s)$	components i in feed node s having specified flows
K	temperature intervals k in the transshipment model for heat integration
L	all streams l between nodes
Lq	intermediate solid product streams
Lw	solid product streams
S	all thermodynamic state nodes: feeds, products, multiple saturation points or operation points, and intermediate solute products
S_F	feed nodes
S_I	intermediate product nodes
S_M	multiple saturation point nodes
$S^{\text{in}}(s), S^{\text{out}}(s)$	input, output streams of node s
$S_d^{\text{in}}, S_d^{\text{out}}$	solid input, output streams of node s
S_s^{out}	solvent output streams from node s
$T(s)$	conditional tasks t for multiple saturation point node s

Variables

$Cf_{l,e}, Cvl_e$	fixed, variable cost incurred for wash stage e
$FC_{t,s}, VC_{t,s}$	fixed, variable cost incurred for equipment associated with task t in node s
$G_{l,t}^{\text{in}}, G_{t,l}^{\text{out}}$	mass flow rates from stream l to task t , from task t to stream l
$hx_{l,i}$	mass flow of component i in the residual liquor retained in the cake pores of stream l
$Qr_{l,e}, Qwl_e$	mass flow rate of wash solvent in reslurry/filter, wash step for solid stream l at stage e
$Q_{t,s}^C$	crystallization or dilution heat duty in task t in node s
$Q_{t,s}^S$	evaporation heat duty in task t in node s
Q_m^V, Q_n^U	use of hot utility m , cold utility n in heat transshipment model
R_k	heat residual exiting temperature interval k in heat transshipment model
w_l	mass flow rate for stream l
w_l^0	mass flow rate of solid in product stream l
$y_{t,s}$	0–1 choice of task t within node $s \in S_M$
ym_l	0–1 choice of intermediate solid product output to steam l
$ywl_{l,e}, yr_{l,e}$	0–1 choice of wash, reslurry/filter for solid product stream l at stage e
$yl_{e,i}$	concentration of species i in the residual mother liquor of solid stream l at the output of wash/reslurry stage e
$zl_{e,i}, rl_{e,i}$	input, output concentration in the washing liquid for solid stream l at stage e
$ypwl_{l,e,i}, ypr_{l,e,i}, ymw_{l,e,i}, ymr_{l,e,i}, zw_{l,e,i}, zr_{l,e,i}, rw_{l,e,i}, rr_{l,e,i}$	concentration of component i in the internal stream of wash stage e as identified in Fig. 2

Parameters

$\alpha_{t,s}$	fixed cost for task t in node s
$\beta_{t,s}$	variable cost coefficient for task t in node s
$c_{t,s}^C, c_{t,s}^S$	unit cost for heat duty $Q_{t,s}^C, Q_{t,s}^S$
Cfw, Cfr, Cff	fixed costs for wash, reslurry, filter operation
Cvw, Cvr, Cvf	variable cost coefficient for wash, reslurry, filter operation
Cs	unit cost of wash solvent use
$C_{s,l}^F$	required flow rate of species i in feed s
$(C_p \Delta T)_{lk}^H, (C_p \Delta T)_{lk}^C$	heat content per unit mass of hot stream $l \in H_k$, cold stream $l \in C_k$ in temperature interval k

$Ew_{l,e,i}, Er_{l,e,i}$	wash, reslurry efficiency parameter for species i in solid stream l at stage e
h_l	mass ratio of retained residual liquor to solid in product stream l
$HQ_{t,s}^C, HQ_{t,s}^D, HS_{t,s}$	crystallization, dissolution, evaporation heats per unit mass in task t in node s
$\Pi_{l,i}$	impurity level of component i in last wash stage \bar{E} for product stream l
$nw_{l,e}, nr_{l,e}$	mass ratio of wash liquid to cake residual liquor in the wash, reslurry/filter step
$x_{l,i}$	concentration of component i in stream l
$x_{p,i}$	concentration of i in the mother liquor in equilibrium with solid product stream l

wash network. A MILP formulation is developed for each network to select the optimum flowsheet alternative for the separation. The first three networks are described in previous references, so emphasis here will be given to the cake wash network.

2.1. Thermodynamic state network

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, by Cisternas (1999) for multicomponent systems, and by Cisternas et al. (2003) for metathetical salts. Fig. 1 shows an example of a thermodynamic state network representation for a two solute system at two temperatures. The structure illustrates a feed, two multiple saturation points, an intermediate product, and two end products. Each multiple saturation point node has three output arcs, representing solid product, saturated solution, and solvent.

tion of this kind of network is described in the above references.

The mathematical formulation for the thermodynamic state network is similar to that developed by Cisternas (1999) and Cisternas et al. (2003), but the present model also includes the residual liquor retained in the cake pores. First, the set of thermodynamic state nodes is 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 (the solutes and solvents) are denoted by the set $I = \{i\}$. The arcs, which denote streams between nodes, are denoted by $L = \{l\}$. Each stream l is associated with the positive mass flow rate variable w_l and with the composition parameters $x_{l,i}$ for each component. The following constraints apply:

- (a) Mass balance for each component in multiple saturation nodes (S_M):

$$\sum_{l \in L_Q \cap S^{\text{in}}(s)} h x_{l,i} + \sum_{l \in S^{\text{in}}(s)} w_l x_{l,i} - \sum_{l \in S^{\text{out}}(s)} w_l x_{l,i} - \sum_{l \in (L_w \cup L_q) \cap S^{\text{out}}(s)} w_l h_l x_{p,i} = 0, \quad s \in S_M, i \in I \quad (1)$$

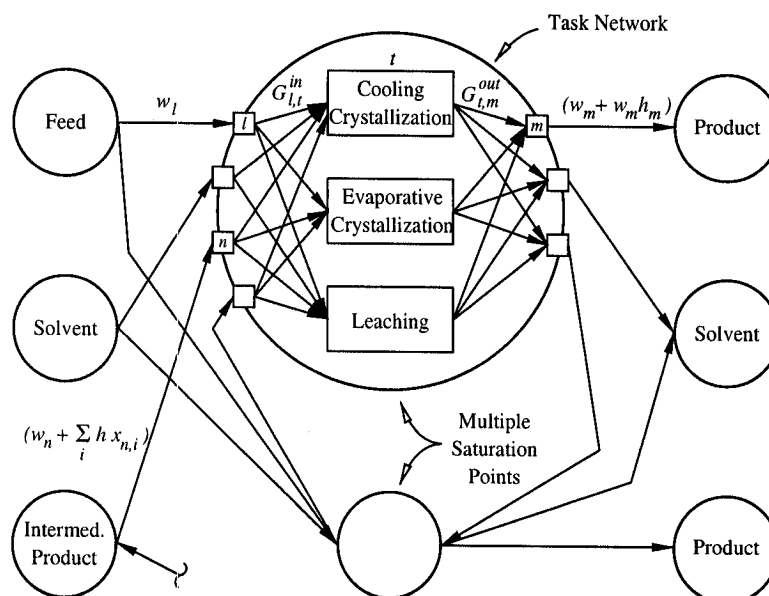


Fig. 1. Thermodynamic state network and a nested task network.

where L_q is the subset of L of the intermediate solid product streams, $hx_{l,i}$ a variable representing the mass flow of component i in the residual liquor retained in the cake pores of stream l , L_w the subset of L of the solid product streams, h_l the mass ratio of residual liquor retained in the cake pores to the solid product l , and $x_{l',i}$ is the concentration of the mother liquor in equilibrium with solid product l . Respectively, $S^{\text{in}}(s)$ and $S^{\text{out}}(s)$ are the sets of input and output streams of node s .

(b) Mass balance for each component in intermediate product nodes (S_I):

$$\sum_{l \in L_q \cap S^{\text{in}}(s)} w_l x_{l,i} - \sum_{l \in L_q \cap S^{\text{out}}(s)} w_l x_{l,i} = 0, \quad s \in S_I, \quad i \in I \quad (2)$$

$$\sum_{l \in L_q \cap S^{\text{out}}(s)} hx_{l,i} - \sum_{l \in L_q \cap S^{\text{in}}(s)} w_l h_l x_{l',i} = 0, \quad s \in S_I, \quad i \in I \quad (3)$$

$$\sum_{i \in I} (w_l x_{l,i} + hx_{l,i}) - U_l y_m \leq 0, \quad l \in L_q \cap S^{\text{out}}(s), \quad s \in S_I \quad (4)$$

$$\sum_{l \in L_q \cap S^{\text{out}}(s)} y_m - 1 = 0, \quad s \in S_I \quad (5)$$

Eq. (2) is the mass balance of each solid, whereas Eq. (3) is the mass balance for residual liquor retained in the cake pores. Washing is not included for intermediate solid products because these streams are recycled back to the process. Eqs. (4) and (5) employ binary variables y_m to restrict the number of output streams from intermediate product nodes to one, but several input streams are allowed.

(c) Specification for feeds flow rates in feed nodes (S_F):

$$\sum_{l \in S^{\text{out}}(s)} w_l x_{l,i} = C_{s,i}^F, \quad s \in S_F, \quad i \in I_F(s) \quad (6)$$

where $C_{s,i}^F$ is the required flow rate of species i in feed s .

$$\begin{bmatrix} y_{t,s} \\ \text{FC}_{t,s} = \alpha_{t,s} \\ \text{VC}_{t,s} = \beta_{t,s} \sum_{l \in S^{\text{in}}(s)} G_{l,t}^{\text{in}} \\ Q_{t,s}^C = \text{HQ}_{t,s}^C G_{t,l}^{\text{out}} + \text{HQ}_{t,s}^D G_{l2,t}^{\text{in}}, \quad l1 \in S_d^{\text{out}}(s), \quad l2 \in S_d^{\text{in}}(s) \\ Q_{t,s}^S = \text{HS}_{t,s} G_{t,l}^{\text{out}}, \quad l \in S_s^{\text{out}}(s) \end{bmatrix} \vee \begin{bmatrix} -y_{t,s} \\ \text{FC}_{t,s} = 0 \\ \text{VC}_{t,s} = 0 \\ Q_{t,s}^C = 0 \\ Q_{t,s}^S = 0 \end{bmatrix}, \quad t \in T(s), \quad s \in S_M(s) \quad (10)$$

$$g(y_{t,s}) = \text{True}$$

2.2. Task networks

A challenging aspect of fractional crystallization process synthesis is that several potential operations, like leaching,

cooling crystallization, and evaporative crystallization, can occur at the same equilibrium condition. Therefore, when a multiple saturation point is selected as an operation point, it also is necessary to select which kind of operation is to be performed at that point. The task network performs this selection. The first multiple saturation point in Fig. 1 shows its task network; a task network must be included for each multiple saturation point. Task selection depends on the characteristics of the input and output streams. 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. (An example is the decomposition of carnallite to form potassium chloride.)

A task network is constructed for each multiple saturation point node s . The formulation is close to that in Cisternas et al. (2001) and includes mass and energy balances, logic relations to select the task based on input/output stream characteristics, and cost evaluations. Let $T(s) = \{t\}$ define the set of conditional tasks in multiple saturation point node $s \in S_M$. The equations are as below.

(d) Mass balance between the thermodynamic state network and task network:

$$w_l + \sum_{i \in I} hx_{l,i} = \sum_{t \in T(s)} G_{l,t}^{\text{in}}, \quad l \in S^{\text{in}}(s), \quad s \in S_M \quad (7)$$

$$w_l + w_l h_l = \sum_{t \in T(s)} G_{t,l}^{\text{out}}, \quad l \in S^{\text{out}}(s), \quad s \in S_M \quad (8)$$

where $G_{l,t}^{\text{in}}$, and $G_{t,l}^{\text{out}}$, are variables representing the internal mass flow rates from stream l to task t , and from task t to stream l , respectively.

(e) Mass balance in the task network:

$$\sum_{l \in S^{\text{in}}(s)} G_{l,t}^{\text{in}} - \sum_{l \in S^{\text{out}}(s)} G_{t,l}^{\text{out}}, \quad t \in T, \quad s \in S_M \quad (9)$$

(f) Task selection and energy balance:

where $y_{t,s}$ represents the choice of task t within each node $s \in S_M$. $\text{FC}_{t,s}$, and $\text{VC}_{t,s}$, are the variable and fixed costs incurred for each equipment item associated with task t . $\text{HQ}_{t,s}^C$, $\text{HQ}_{t,s}^D$, and $\text{HS}_{t,s}$ are parameters representing the

crystallization, dissolution, and evaporation heats per unit mass in each task t . The corresponding heat duties $Q_{t,s}^C$ (crystallization or dilution) and $Q_{t,s}^S$ (evaporation) have unit costs $c_{t,s}^C$ and $c_{t,s}^S$, respectively. S_d^{out} is the subset of L of the solid outputs from node $s \in S_M$, S_d^{in} is the subset of L of solid inputs to node $s \in S_M$, and S_s^{out} is the subset of L of solvent outputs from node $s \in S_M$. $g(y_{t,s})$ represents the logic relations between Boolean variables to make the task selection consistent with input/output stream properties. Eq. (10) is transformed into mixed-integer linear form.

2.3. Heat integration network

Crystallization requires much less energy for separation that does distillation, but energy costs can have an impact on process economics and process design (Rajagopal, Ng, & Douglas, 1988). The third network provides heat integration. Here a heat exchange network is included, represented as a transshipment problem as in Papoulias and Grossmann (1983), and formulated as a linear programming problem. The hot streams (source nodes) and cold streams (destination nodes) in the formulation correspond to the arc flows in the thermodynamic state network.

First, a set $K = \{k\}$ of temperature intervals is formed based on the process stream inlet temperatures and those utility stream inlet temperatures that fall within the temperature range of the process streams. The only constraints that apply are:

(g) Heat balance around each temperature interval k :

$$R_k - R_{k-1} - \sum_{m \in V_k} Q_m^V + \sum_{n \in U_k} Q_n^U = \sum_{l \in H_k} w_l (C_p \Delta T)_{lk}^H - \sum_{l \in C_k} w_l (C_p \Delta T)_{lk}^C, \quad k \in K \quad (11)$$

where Q_m^V , Q_n^U , and R_k are positive variables that represent the heat load of hot utility m , the heat load of cold utility n , and the 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 . H_k , C_k , V_k , and U_k are the hot stream, cold stream, hot utility, and cold utility sets, respectively, in interval k .

2.4. Cake wash network

The fourth network is the cake wash network. Cake washing can be accomplished by two methods: (a) The cake may be washed prior to removal from the filter by flushing with washing liquor. This can be done with both batch and continuous filters. (b) The cake may be removed from the filter and then washed in a mixer. The wash suspension obtained may then be separated on the filter. Fig. 2 shows both alternatives for removing the residual mother liquor of concentration y_{e-1} . Fig. 2 shows only one stage, but washing may be performed in one or several stages on either batch or continuous filters. In this work countercurrent washing is not considered. As a result, the first stage produces the most concentrated solution and the last stage produces the least. If operation states are equilibrium states, then mother liquor concentration in the cake is substantially that of a saturated solution at the final temperature in the crystallization process.

Ideally, washing would be continued until the concentration of solute in the cake has fallen to some acceptable level, or until the maximum allowable degree of dilution of the collected filtrate has been reached. Residual liquor is usually removed by one of three methods: (i) simple displacement washing, (ii) reslurrying of the cake with wash liquid followed by refiltering, and (iii) counter-current washing. The first two methods are considered here.

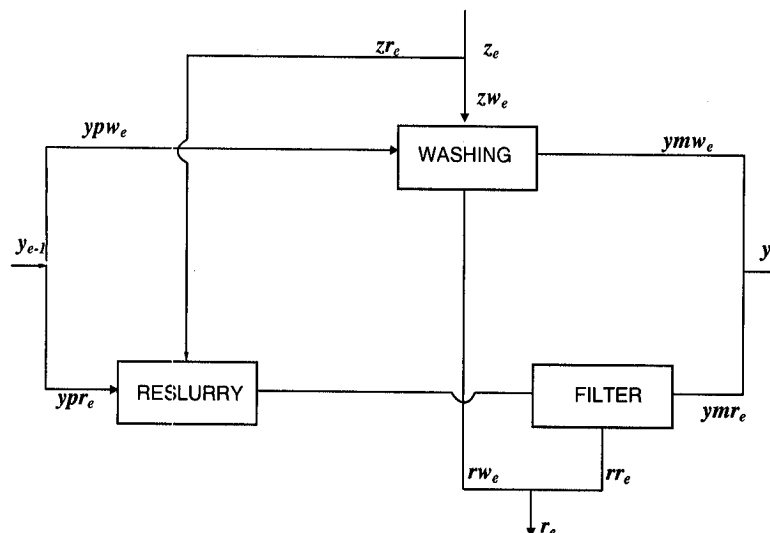


Fig. 2. Cake wash network for stage e .

A cake wash network is constructed for each solid stream product $l \in Lw$. Let $E(Lw) = \{e\}$ define the set of washing/reslurry stages for the solid stream products $l \in Lw$. The network for one stage e is shown in Fig. 2. Note that each solid stream product can have several networks in series like the one shown in Fig. 2. The variables are defined as follows: $y_{l,e,i}$ is the concentration of species i in the residual mother liquor of solid stream l at the output of wash/reslurry stage e . $z_{l,e,i}$ and $r_{l,e,i}$ are the input and output concentrations in the washing liquid for the solid stream l at stage e . $ypw_{l,e,i}$, $ypr_{l,e,i}$, $ymw_{l,e,i}$, $ymr_{l,e,i}$, $zwl_{l,e,i}$, $zrl_{l,e,i}$, $rw_{l,e,i}$, and $rr_{l,e,i}$, are the concentrations of the internal streams

$$\begin{aligned} Ew_{l,e,i}rw_{l,e,i} - Ew_{l,e,i}ypw_{l,e,i} - ymw_{l,e,i} + ypw_{l,e,i} &= 0 \\ Er_{l,e,i}rr_{l,e,i} - Er_{l,e,i}ypr_{l,e,i} - ymr_{l,e,i} + ypr_{l,e,i} &= 0 \end{aligned}, \quad l \in Lw, e \in E(Lw), i \in I \quad (14)$$

in stage e as identified in Fig. 2. The first constraints that apply are:

(h) Mass balance for each component in wash/reslurry stage:

$$\begin{aligned} ypw_{l,e,i} + nw_{l,e}zwl_{l,e,i} - ymw_{l,e,i} - rw_{l,e,i}nw_{l,e} &= 0 \\ ypr_{l,e,i} + nr_{l,e}zrl_{l,e,i} - ymr_{l,e,i} - rr_{l,e,i}nr_{l,e} &= 0 \end{aligned}, \quad l \in Lw, e \in E(Lw), i \in I \quad (12)$$

where $nw_{l,e}$ and $nr_{l,e}$ are parameters that represent the mass ratio of wash liquid to residual liquor in the cake used in the wash and reslurry/filter steps, respectively. These ratios are referred to as the wash ratio or number of displacements.

$$\begin{aligned} \left[\begin{array}{l} yw_{l,e} \\ -yr_{l,e} \\ y_{l,e,i} = ymw_{l,e,i} \\ ypw_{l,e,i} = y_{l,e-1,i} \\ ymr_{l,e,i} = 0 \\ ypr_{l,e,i} = 0 \\ zw_{l,e,i} = z_{l,e,i} \\ zr_{l,e,i} = 0 \\ Qw_{l,e} = nw_{l,e}h_lw_l^0 \\ Qr_{l,e} = 0 \\ Cf_{l,e} = Cfw \\ Cv_{l,e} = CvwQw_{l,e} + CsQw_{l,e} \end{array} \right] \vee \left[\begin{array}{l} -yw_{l,e} \\ yr_{l,e} \\ y_{l,e,i} = ymr_{l,e,i} \\ ypr_{l,e,i} = y_{l,e-1,i} \\ ymw_{l,e,i} = 0 \\ ypw_{l,e,i} = 0 \\ zw_{l,e,i} = 0 \\ zr_{l,e,i} = z_{l,e,i} \\ Qw_{l,e} = 0 \\ Qr_{l,e} = nr_{l,e}h_lw_l^0 \\ Cf_{l,e} = Cfr + Cff \\ Cv_{l,e} = Cvr(Qr_{l,e} + w_l^0)CvfQr_{l,e} + CsQr_{l,e} \end{array} \right] \vee \left[\begin{array}{l} -yw_{l,e} \\ -yr_{l,e} \\ y_{l,e,i} = y_{l,e-1,i} \\ ymr_{l,e,i} = 0 \\ ypr_{l,e,i} = 0 \\ ymw_{l,e,i} = 0 \\ ypw_{l,e,i} = 0 \\ zw_{l,e,i} = 0 \\ zr_{l,e,i} = z_{l,e,i} \\ Qw_{l,e} = 0 \\ Qr_{l,e} = 0 \\ Cf_{l,e} = 0 \\ Cv_{l,e} = 0 \end{array} \right], \quad e \in E(Lw), l \in Lw, i \in I \quad (15)$$

In the ideal case, for a single washing only one void volume of wash liquor is required for 100% recovery in the residual liquor. In practice, only 30–86% of the retained filtrate is removed by a one-displacement wash (Wakeman, 1980). In this work, the wash efficiency parameter $Ew_{l,e,i}$ for species i in solid stream l at stage e is defined as

$$Ew_{l,e,i} = \frac{ymw_{l,e,i} - ypw_{l,e,i}}{rw_{l,e,i} - ypw_{l,e,i}}, \quad l \in Lw, e \in E(Lw), i \in I \quad (13)$$

The reslurry/filter case is treated with an analogous efficiency $Er_{l,e,i}$. Note that for perfect mixing in the wash mixer the efficiency is equal to 1. This definition of efficiency treats cake washing in terms of mixing wash liquor and residual filtrate in the entire pore volume of the cake, not recognizing that washing is a mass transfer process governed by molecular diffusion and dispersion kinetics. A more fundamental modeling of cake washing is developed in Wakeman (1980). Rewriting Eq. (13) for the two cases, we have the following two constraints:

(i) Efficiency constraint for wash/reslurry stage:

This network requires the use of discrete variables $yw_{l,e}$ and $yr_{l,e}$ to represent the choices of wash or reslurry/filter for each solid product stream $l \in Lw$ at stage e . Also,

relationships are needed to connect each stage and to include costs of the washing and reslurry/filter stages.

(j) Wash or reslurry/filter selection:

In this equation, $Cf_{l,e}$ and $Cv_{l,e}$ are the fixed and variable costs for stage e . $Qr_{l,e}$ and $Qw_{l,e}$ are the mass flow rates of wash solvent in the reslurry/filter and wash steps in stage e for the solid product l . Cfw , Cfr , and Cff are the fixed costs for the wash, reslurry, and filter operations, and Cvw , Cvr , and Cvf are the corresponding variable cost coefficients. Cs is the unit cost of the wash solvent use. w_l^0 is the mass flow rate of solid in product l . This value is an approximation to w_l , which itself can be calculated easily by mass balance, but using the approximation allows us to keep the

model linear. Eq. (15) is rewritten in mixed-integer linear form.

The concentration of the last stage \bar{E} must satisfy the impurity level $IL_{l,i}$.

(k) Degree of impurity:

$$y_{l,\bar{E},i} h_l \leq IL_{l,i}, \quad l \in Lw, i \in I \quad (16)$$

2.5. Objective function

The objective function minimizes the total venture cost

$$\min \sum_{s \in S_M} \sum_{t \in T(s)} (FC_{t,s} + VC_{t,s} + c_{t,s}^C Q_{t,s}^C + c_{t,s}^S Q_{t,s}^S) + \sum_{m \in V} c_m Q_m^V + \sum_{n \in U} c_n Q_n^U + \sum_{l \in Lw} \sum_e (Cf_{l,e} + Cv_{l,e}) \quad (17)$$

Eq. (17) includes the annualized investment cost and utility and solvent use costs. The objective function in Eq. (17), subject to the constraints in Eqs. (1)–(16), defines a mixed-integer linear programming problem. The numerical solution to this MILP problem can be obtained with standard algorithms, yielding the simultaneous solution of the coupled networks.

Table 1
Data and parameters for sylvinitic example

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
Feed rate (sylvinitic)	100,000 t per year
Heat capacities	
Water	1.00 Mcal/(t °C)
Hot streams	0.84 Mcal/(t °C)
Cold streams	0.81 Mcal/(t °C)
Latent heat of vaporization	586.602 Mcal/t at 20 °C, 539.421 Mcal/t at 100 °C
Crystallization/dissolution heat	
KCl	±59.114 Mcal/t
NaCl	±19.897 Mcal/t
Fixed cost coefficients, α_i	
Cooling crystallization	US\$ 20,000 per year
Evaporative crystallization	US\$ 27,636 per year
Leaching	US\$ 681 per year
Variable cost coefficients, β_i	
Cooling crystallization	US\$ 0.2200 per t per year
Evaporative crystallization	US\$ 0.5570 per t per year
Leaching	US\$ 0.0229 per t per year
Utility cost	
Steam	US\$ 0.0102 Mcal ⁻¹
Cooling water	US\$ 0.0018 Mcal ⁻¹

Table 2
Equilibrium data for carnallite example

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 ·6 H ₂ O + carnallite
H1	105	7.00	30.82	KCl + carnallite
H2	105	1.07	40.75	MgCl ₂ ·6 H ₂ O + carnallite

3. Illustrative examples

3.1. Design of sylvinitic separation system

This example considers the production of potassium chloride from 100,000 t per year of sylvinitic (47.7% KCl, 52.3% NaCl). Problem data and parameters from Cisternas et al. (2001) are given in Table 1. A fixed cost for washing was not considered, whereas the variable cost of washing includes a solvent cost (US\$ 0.81 per t). The fixed cost for reslurrying/filtering was taken as US\$ 6759 per year, while the variable cost coefficients for reslurrying and filtering were US\$ 0.31 per t and US\$ 0.24 per t, respectively, plus the solvent cost. The maximum allowed impurity levels were 0.009 kg NaCl/kg solvent in the KCl cake and 0.01 kg KCl/kg solvent for the NaCl cake. The MILP formulation contains 299 equations, 218 continuous variables, and 27 binary variables.

The solution obtained is shown in Fig. 3. This is the same basic structure found by Cisternas et al. (2001), where both NaCl and KCl are obtained by leaching. However, the

Table 3
Thermal properties and cost parameters for carnallite example

Feed rate carnallite	100,000 t per year
Heat capacities	
Water	1.00 Mcal/(t °C)
Hot streams	0.84 Mcal/(t °C)
Cool streams	0.81 Mcal/(t °C)
Temp/latent heat of vaporization for water	35 °C/578.165 Mcal/t, 105 °C/536.099 Mcal/t
Crystallization/dissolution heat (+/-)	
KCl	59.114 Mcal/t
MgCl ₂ ·6H ₂ O	-35.675 Mcal/t
Carnallite	55.807 Mcal/t
Fixed cost coefficients, α_i	
Cooling crystallization step	US\$ 11,200 per year
Evaporative crystallization step	US\$ 4800 per year
Reactive crystallization step	US\$ 33,066 per year
Variable cost coefficients, β_i	
Cooling crystallization step	US\$ 0.205 per t per year
Evaporative crystallization step	US\$ 0.9205 per t per year
Reactive crystallization step	US\$ 0.584 per t per year
Steam cost	US\$ 0.0102 Mcal ⁻¹
Cooling water cost	US\$ 0.0018 Mcal ⁻¹

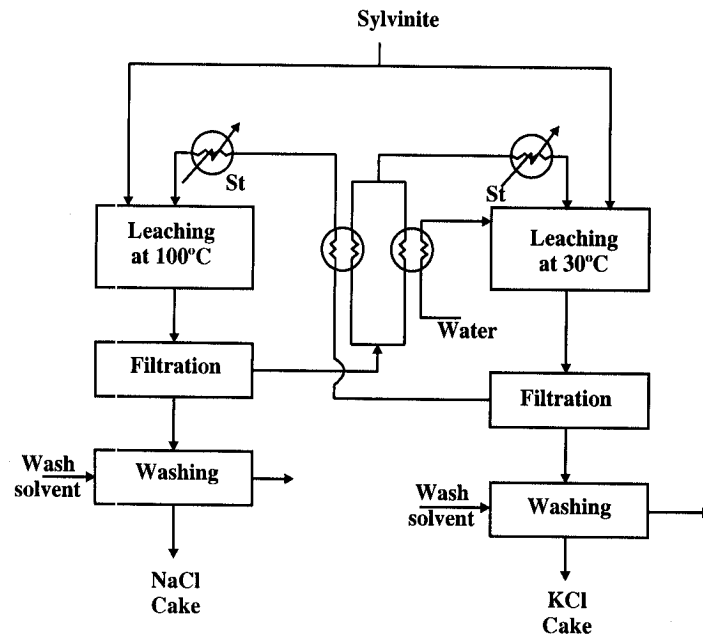


Fig. 3. Flowsheet solution for sylvinite example.

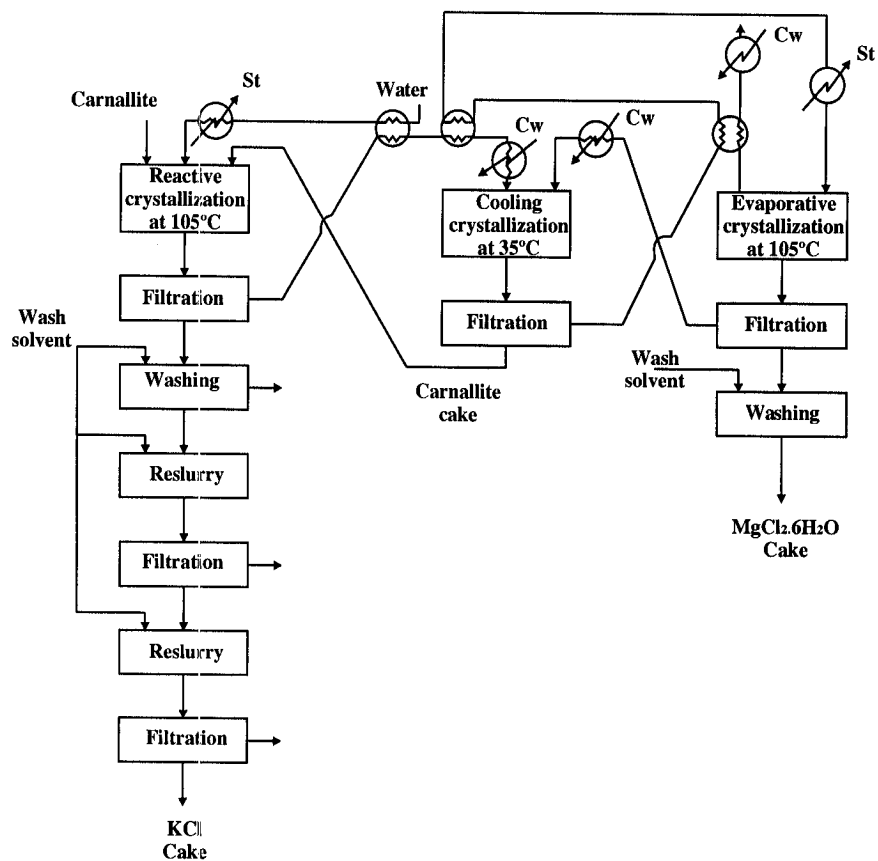


Fig. 4. Flowsheet solution for carnallite example.

Table 4
Equilibrium data for astrakanite example

Key	Temperature (°C)	Saturated solution (wt.%)		Solid phase
		MgSO ₄	Na ₂ SO ₄	
C1	18.7	20.57	11.80	MgSO ₄ ·7H ₂ O + Na ₂ SO ₄ ·10H ₂ O
C2	25	21.15	13.00	MgSO ₄ ·7H ₂ O + astrakanite
C3	25	16.60	17.80	Astrakanite + Na ₂ SO ₄ ·10H ₂ O
H1	50	31.32	4.74	MgSO ₄ ·6H ₂ O + astrakanite
H2	50	11.98	23.25	Astrakanite + Na ₂ SO ₄
H3	97	32.20	5.55	MgSO ₄ ·H ₂ O + MgSO ₄ ·Na ₂ SO ₄
H4	97	14.40	19.15	MgSO ₄ ·Na ₂ SO ₄ + MgSO ₄ ·3Na ₂ SO ₄
H5	97	5.88	26.90	MgSO ₄ ·3Na ₂ SO ₄ + Na ₂ SO ₄

solution obtained here includes wash stage selection. Varying the residual liquor retention parameter over the range of 0.0–0.10 shows that the solution cost can be affected by 20%. Varying the allowed product impurity levels over the range of 0.007–0.05 produces a cost variation of similar magnitude.

3.2. Design of carnallite decomposition

The problem consists of separating potassium chloride and magnesium chloride from 100,000 t per year of the double salt carnallite, KCl·MgCl₂·6H₂O. Problem data from Cisternas et al. (2001) are given in Tables 2 and 3. Fixed and variable cost coefficients for washing, reslurrying, and filtering were the same as used in the sylvinite example above. The maximum allowed impurity levels were 0.0005 kg MgCl₂/kg solvent in the KCl cake and 0.001 kg KCl/kg solvent for the MgCl₂·6H₂O cake. The MILP formulation contains 598 equations, 556 continuous variables, and 69 binary variables.

The solution found is shown in Fig. 4. This is the same basic configuration found by Cisternas et al. (2001), where KCl is obtained by reactive crystallization and MgCl₂ is obtained by evaporative crystallization, but in addition includes wash stage selection. One wash step and two reslurry/filter steps were needed for the KCl cake because very little MgCl₂ was allowed in this cake.

3.3. Design of astrakanite decomposition

The problem consists in the production of MgSO₄ and Na₂SO₄ from 100,000 t per year of astrakanite, MgSO₄·Na₂SO₄·4H₂O. Equilibrium data from Linke and Seidell (1965) for four temperatures are shown in Table 4. In the case of the sylvinite separation presented above, it is possible to only consider two potential separation temperatures because the solid phases in equilibrium with each multiple saturation point are always the same. Then, if the difference between the relative composition at the cold and hot operation temperature increases, the total flow rate in the process will decrease (Cisternas & Rudd, 1993). However, that rule cannot be applied in this example because

the solid phases that will exist change with temperature. At 18.7 °C, there are only two solid phases. However, at 25 and 50 °C there are three solid phases, and therefore two multiple saturation points at each temperature. At 97 °C

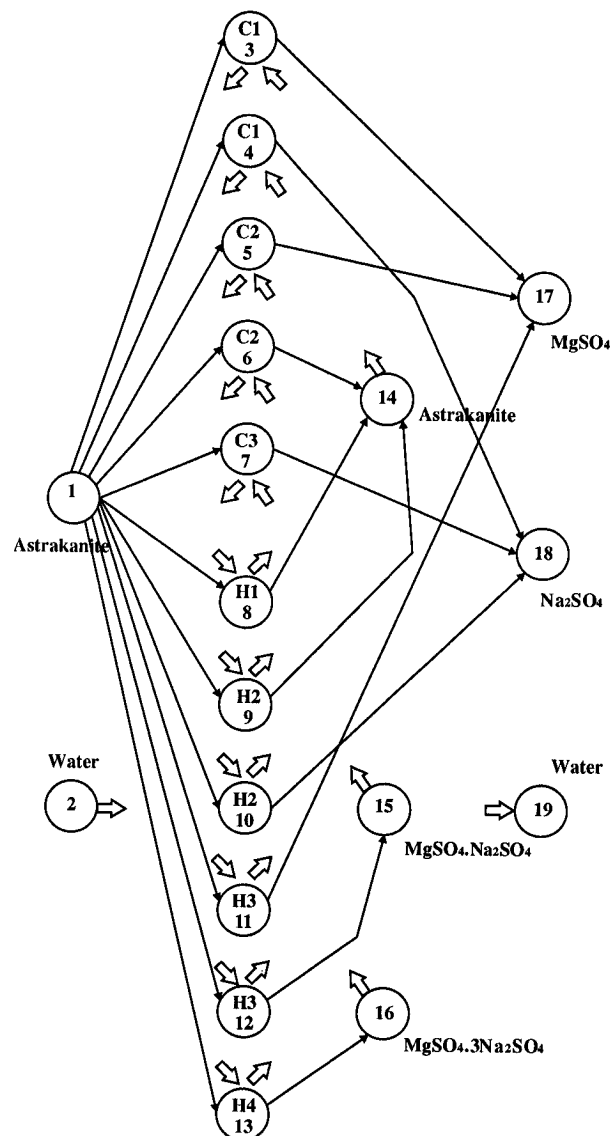


Fig. 5. Thermodynamic state network for astrakanite example.

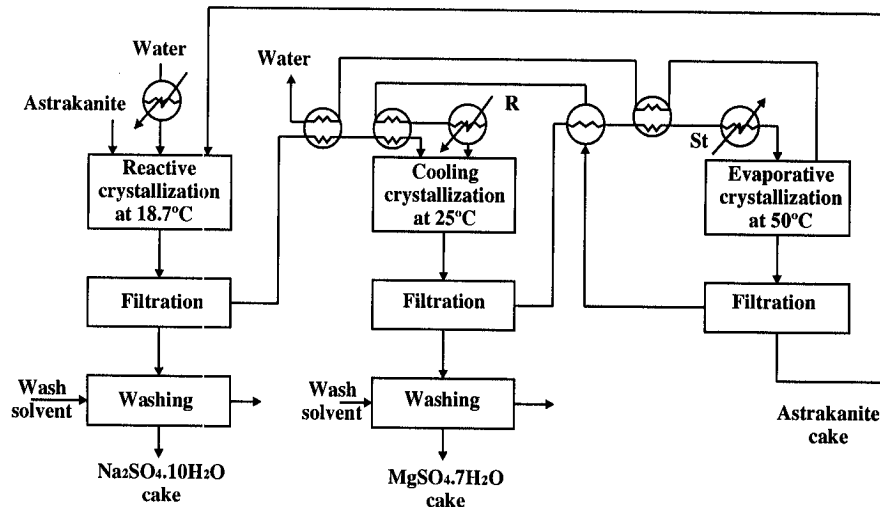


Fig. 6. Flowsheet solution for astrakanite example.

there are four solid phases, and therefore three multiple saturation points. The thermodynamic state network, Fig. 5, can be constructed on the basis of relative compositions as described by Cisternas (1999). The open arrows in Fig. 5 represent the numerous feasible paths interconnecting the

Table 5
Thermal properties and cost parameters for astrakanite example

Feed rate (astrakanite)	100,000 t per year
Heat capacities	
Water	1.00 Mcal/(t °C)
Hot streams	0.84 Mcal/(t °C)
Cold streams	0.81 Mcal/(t °C)
Latent heat of vaporization	587.289 Mcal/t at 18.7 °C, 575.132 Mcal/t at 25.0 °C, 569.505 Mcal/t at 50.0 °C, 541.335 Mcal/t at 97.0 °C
Crystallization/dissolution heat	
MgSO ₄ ·7H ₂ O	±12.907 Mcal/t
Na ₂ SO ₄ ·10H ₂ O	±58.187 Mcal/t
Astrakanite	±51.311 Mcal/t
Fixed cost coefficients, α_i	
Cooling crystallization	US\$ 11,200 per year
Evaporative crystallization	US\$ 4800 per year
Reactive crystallization	US\$ 33,066 per year
Reslurry	US\$ 95 per year
Filtration	US\$ 6664 per year
Variable cost coefficients, β_i	
Cooling crystallization	US\$ 0.205 per t per year
Evaporative crystallization	US\$ 0.921 per t per year
Reactive crystallization	US\$ 0.584 per t per year
Reslurry	US\$ 0.310 per t per year
Filtration	US\$ 0.240 per t per year
Utility cost	
Steam	US\$ 0.0102 Mcal ⁻¹
Cooling water	US\$ 0.0018 Mcal ⁻¹
Refrigeration	US\$ 0.0283 Mcal ⁻¹
Washing solvent	US\$ 0.81 per t

multiple saturation point nodes that for clarity are not shown explicitly. The thermodynamic state network has 11 multiple saturation nodes and 3 double salt or intermediate product nodes. There are 83 arcs representing 83 potential streams. The MILP formulation contains 1209 equations, 1201 continuous variables, and 145 binary variables. Solution time was 84 s for OSLv2 (GAMS) with a 1.7 GHz Pentium 4 processor.

The solution obtained using the problem parameters of Table 5 is shown in Fig. 6. Three operation temperatures are selected. Na₂SO₄·10H₂O is produced by decomposition of astrakanite, whereas MgSO₄·7H₂O is produced by cooling crystallization. Evaporative crystallization is utilized to recycle astrakanite. Both cakes were washed; in the Na₂SO₄·10H₂O cake, the mass ratio of wash liquid to residual liquor was 1 and the impurity level was 0.014 kg MgSO₄/kg solvent (maximum allowed was 0.015). In the MgSO₄·7H₂O cake, the mass ratio of wash liquid to residual liquor was 3 and the impurity level was 0.004 kg Na₂SO₄/kg solvent (maximum allowed was 0.005). The astrakanite cake was not washed because this intermediate product is recycled back to the reactive crystallization of Na₂SO₄·10H₂O. Low temperature operation is selected, so it is necessary to use refrigeration (indicated by R in Fig. 6).

4. Conclusions

A method for determining the desired process flowsheet for fractional crystallization processes is presented here that explicitly incorporates the decisions and effects of cake washing operations. The synthesis model is comprised of coupled networks of four types: the thermodynamic state network, corresponding task networks, the heat integration network, and the cake wash network. Once the representation is specified, the problem is formulated and easily solved as a MILP. The test examples show that the model can be

useful in the design and study of fractional crystallization processes. The sensitivity of the optimal cost to changes in the values specified for product impurity levels and the level of residual liquor retained in the cake also can be seen.

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