Optimal Design of Crystallization-Based Separation Schemes

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A network flow model is presented for synthesizing crystallization-based separations for multicomponent systems. The construction of the network flow is based on the identification of feasible thermodynamic states. The method allows consideration of several operation temperatures, complex solid−liquid equilibrium behavior, and several multicomponent feeds and products. For systems with two solutes a linear programming model is obtained, while for systems with three or more solutes a nonlinear programming model is obtained. The relative composition diagram is proposed to determine feasible operation points. For a small problem the relative composition diagram can be used to recognize flowsheet alternatives. For large problems, the relative composition diagram allows one to decrease the nodes in the network, thus decreasing the execution time. The technique is illustrated with three example problems.

Introduction

Multicomponent separation sequences are an important part of almost all chemical processing systems. Because of the significant role that separation processes play in the total capital investment and annual operating cost for a chemical plant, a great deal of interest has been generated in the development of systematic approaches that will select optimum separation sequences.

Crystallization-based separation has a wide variety of industrial applications, including production of potassium chloride, potassium sulfate, sodium sulfate, potassium nitrate, and sodium chloride (Butts, 1994). The technique consists of sequences of heating, cooling, evaporation, dilution, solventing-out, salting-out, and solid−liquid separations.

Most of the previous research on crystallization-based separation synthesis has focused upon identification and generalization of separation schemes on the phase diagram. Examples of these works are Berry and Ng (1996, 1997), Cisternas and Rudd (1993), Dye and Ng (1995), Ng (1991), and Oyanader et al. (1997). However, several systems are difficult to analyze in the phase diagram. Examples of those systems are (a) systems that have complex solid−liquid equilibrium behavior (formation of several double salts, hydrate and anhydrous salts, etc.); (b) processes with several feeds and product specifications (pure, mixtures, solid, solutions, etc.); (c) processes with several operation temperatures; (d) processes with mixing and division of streams; and (e) systems that have more than two degrees of freedom and are therefore difficult to represent on a phase diagram.

Recently, Cisternas and Swaney (1998) presented a new procedure for the synthesis of crystallization-based separation. The method consists of the construction of a network flow model to represent the set of potential separation flowsheet structures. The solution of the network flow model shows the optimal mass flow pattern between the candidate operation states. The approach presented by Cisternas and Swaney does not need the phase-diagram representation, and therefore complex systems can be studied. However, the method as was presented cannot be applied to systems with three or more solutes, because the method allows only one solid specie to precipitate at each node, and coprecipitation of two or more solids might be needed for systems with three or more solutes. Although the Cisternas and Swaney model can be solved using standard optimization packages, the construction of the network can be difficult to do by hand for complex systems.

This work presents a procedure for the synthesis of crystallization-based separation with two or more solutes. This problem can be stated as follows (Cisternas and Swaney, 1998): Given a set of feeds containing a set of species (solutes and solvents) and a set of allowed candidate operating temperatures, synthesize a process flow sheet that will separate the feed streams into product streams of specified compositions at minimum total cost. The desired products are to be isolated from multicomponent feed streams utilizing fractional crystallization. The procedure is based upon a mathematical programming approach. The basic idea in this approach is to derive a network that has embedded all feasible configurations of separation sequences. The optimal separation sequence that can separate multiple feeds into several multicomponent products is generated by minimizing an objective function expressed in terms of the material flows.

The procedure presented is based on four simple observations. First, the process is represented in a network of nodes and arc. Each node represents a particular thermodynamic state. The crystallization, dissolution, evaporation, dilution, salting-out, and coprecipitation steps are represented in terms of material flows between thermodynamic equilibrium states. Arc represents the material flows between nodes. Second, although practical operations do not operate at a point of multiple saturation, they operate as close as practical to these points to maximize product recovery. Third, the relative composition can be used to reduce the network with no loss of generality. Fourth, investment costs and operating costs of fractional crystallization systems are increasing functions of the evaporation, dilution, and recycle rates.

Synthesis Strategy

The procedure presented for the synthesis of fractional separation sequences consists of the following steps:

(1) The n-component system is divided in all possible $(n-1)$-component systems, and the $(n-1)$-component systems are divided in all possible $(n-2)$-components systems, and so on until two solute systems are reached. A network is derived for each system based on key thermodynamic states as will be explained later. Each network contains unknown stream connections that may determine several arrangements, stream splitting, and stream mixing.

(2) The overall network is then considered to be the aggregate of all networks for each system.

(3) The overall network is formulated as a nonlinear programming (NLP) problem whose objective is to minimize the total cost (in the examples of this article the total flow rate is used as an approximation), and that constrains the mass balances, flow-rate specification, and composition specifications.

(4) The solution to the NLP problem of step 3 provides the optimal separation system, the flow rates of the corresponding streams, and the composition of streams with unknown composition.

The examples show that many streams in the network tend to be deleted, which implies that the selected optimal separation sequence is not a complicated one.

Network Construction

The important feature of the proposed network flow model is that the network can be partitioned into a set of networks that correspond to each combination of solutes. Thus, the n-component system is divided into all combinations of $(n-1)$-component systems, and the $(n-1)$-component systems are divided into all possible $(n-2)$-component systems, and so on until two solute systems are reached. A two-solute system corresponds to a ternary system if the solvent is included. Each system network is derived in such a way that all configurations of interest for the separation process are embedded in it.

First, the construction of a network is explained for a ternary system, and then a quaternary system is used to explain the construction of a network for multicomponent systems.

Ternary systems

A typical partial cycle is shown on the ternary phase equilibrium diagram in Figure 1a (Fitch, 1970). The solvent concentration of the solution at the hot point of multiple saturation H is adjusted by dilution to form point b. When the temperature changes, the solution at point b forms an equilibrium mixture of a salt 2 and a solution at the cold point of multiple saturation C. The solvent concentration of the point C is adjusted by evaporation to get point a, which upon a temperature change forms an equilibrium mixture of salt 1 and a solution at the hot point of multiple saturation H. This completes the partial cycle.

If a feed F is included to complete the cycle, then three alternative process configurations are possible. The first alternative consists of mixing feed F with solution C, and a second alternative consists of mixing feed F with solution H. These alternatives were analyzed by Cisternas and Rudd (1993). Finally, a third alternative consists of splitting the feed into two streams, one to mix with point C and another to mix with point H. This last alternative was analyzed by Cisternas and Swaney (1998).

For any processing cycle to function, two conditions need to be met: (1) the relative compositions at the solutions at the multiple saturation points (H and C) must differ. The relative composition R is defined (Cisternas and Rudd, 1993) as the mass ratio of salt 1 to salt 2. The relative composition at the hot and cold multiple saturation points are denoted R^H and R^C. In Figure 1b, the relative composition is represented by the dilution rays that pass through points H and C. (2) A crystallization step is possible if between the relative composition of the multiple saturation points and the relative composition of the salt in equilibrium with the solution, there is at least another multiple saturation point or intermediate solute point. For example, at the cold multiple saturation point C of Figure 1 salt 2 can be crystallized if the solution H is used as the starting point. On the other hand, at point C it is not possible to crystallize salt 1 because there is no starting point (any point with R between $R^{\text{Salt}1}$ and R^C). In the same way, the hot multiple saturation point H can only be used to crystallize salt 1 if the solution at point C is used as the starting point. Table 1 summarizes these conclusions. Figure 1c shows a diagram with the relative composition of the multiple saturation points and solid phases. This diagram, which will be called the *relative composition diagram*, can be used to arrive at these conclusions more easily.

The diagram of Figure 1c, and therefore Table 1, can be constructed without drawing the phase diagram. This is important when the phase diagram is difficult to construct; for example, when several temperatures want to be considered or the system has more than two solutes.

Since more than one solute may crystallize at a multiple saturation point, operation exactly at these points is not pos-

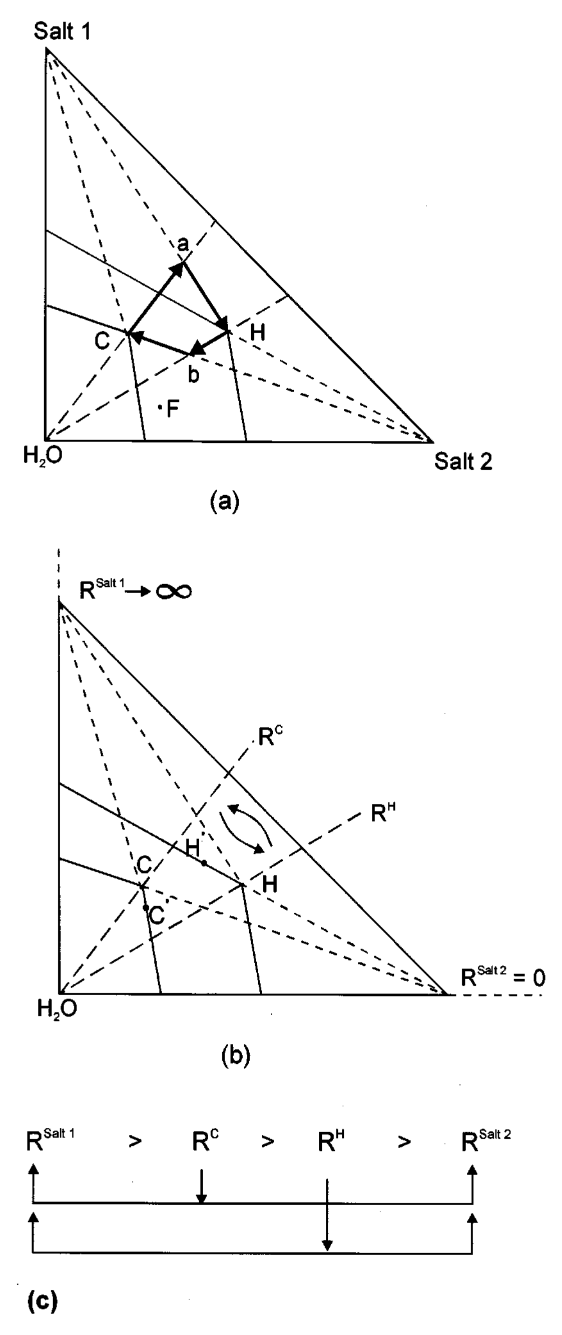

Figure 1. Partial cycle for the separation of salt 1 and salt 2.

(a) Vector path on the phase diagram. (b) Relative compositions. (c) Relative composition diagram.

Table 1. Feasible and Unfeasible Operation for the Phase Diagram of Figure 1

Point	Can Be Used to Precipitate	Starting with Point	Because
C	Salt 2	H	$R^C > R^H > R^{\text{Salt}\,2}$
H	Salt 1	C	$R^{\text{Salt}\,1} > R^C > R^H$
Point	Cannot be Used to Precipitate	Because There is No Starting Point Between	
C	Salt 1	$R^{\text{Salt}\,1}$ and R^C	
H	Salt 2	R^H and $R^{\text{Salt}\,2}$	

sible. Therefore, after the theoretical feasible operation points are selected, practical operation points can be selected near the actual multiple saturation points. For example, in Figure 1b points C' and H' can be used. If the difference between the relative composition of points C' and H' decreases, then the recycle flow rates between these points increase. So, practical operation points must be as close as possible to multiple saturation points. For instance, in Perry et al. (1984), a 95–98% approach is reported as normally possible with inorganic salts. For simplicity, multiple saturation points are used in this work as operation points.

The selection of the operating temperatures can be made so that a significant difference in the relative composition is achieved.

With the information in Table 1 the network of Figure 2 can be constructed. Nodes C and H are the operation points that can produce salt 2 and salt 1, respectively. Water can be added (a dilution or leaching step) or removed (an evaporation step). This network represents three alternatives: (1) feed is mixed with solution H; (2) feed is mixed with solution C; and (3) feed is divided in two streams, one of which is mixed with solution H, while the other is mixed with solution C. The choice between these alternatives depends on the composition of the feed, solution C, and solution H.

Multicomponent systems

The method to be developed in this subsection is similar to the one just used for ternary systems, only more varieties are possible. Because the graphical representation of multicomponent systems is very complicated, the method will be explained in detail only for four-component systems. However, the method applies in general to multicomponent systems.

A four-component system can be represented in a two-dimensional representation if the temperature and pressure are fixed, and if the system is saturated with at least one solid phase. Figure 3 shows the phase equilibrium diagram at two temperatures. All points on this diagram are saturated solutions. Salt 1, salt 2, and salt 3 can be anhydrous or hydrate salt. Isothermal evaporation of any initial solution must end in the point representing a solution saturated with the three substances.

A typical partial cycle for this kind of system is shown in Figure 3a. The solvent and salt-3 concentration of the solution at the hot point of multiple saturation H are adjusted by dilution/evaporation and salting-out, respectively, to form point b. When the temperature changes, the solution at point

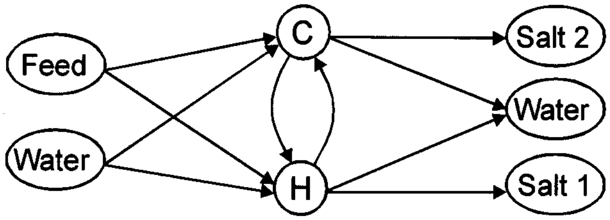

Figure 2. Network structure.

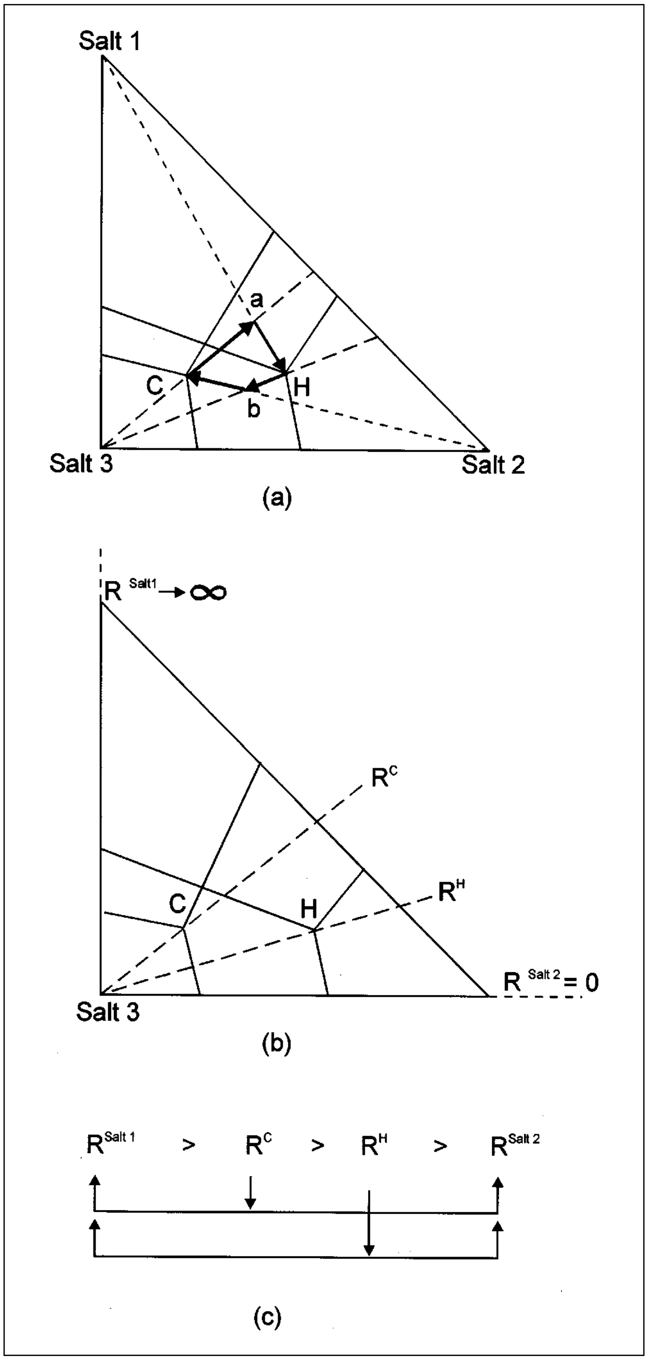

Figure 3. Partial cycle for the separation of salt 1 and salt 2 using salt 3 as pseudosolvent.

(a) Vector path on the phase diagram. (b) Relative composition. (c) Relative composition diagram.

b forms an equilibrium mixture of salt 2 and a solution at the cold point of multiple saturation C. The solvent concentration of point C is adjusted to get point a, which when the temperature changes forms an equilibrium mixture of salt 1, salt 3, and a solution at the hot point of multiple saturation H. This completes the partial cycle. Salt 3 is called the pseudosolvent because it participates in the dissolution or crystallization of other components.

Table 2. Feasible and Unfeasible Operation for the Phase Diagram of Figure 3

Point	Can Be Used to Precipitate	Starting with Point	Because
C	Salt 2 by salting out with salt 3	H	$R^C > R^H > R^{\mathrm{Salt2}}$
C	Salt 2 and salt 3	H	$R^C > R^H > R^{\mathrm{Salt2}}$
H	Salt 1 by salting out with salt 3	C	$R^{\mathrm{Salt1}} > R^C > R^H$
H	Salt 1 and salt 3	C	$R^{\mathrm{Salt1}} > R^C > R^H$
Point	Cannot be Used to Precipitate	Because There is No Starting Point Between	
C	Salt 1	R^{Salt1} and R^C	
H	Salt 2	R^H and R^{Salt2}	

The method follows a similar course to the method for ternary systems: however, since salt 3 can be added (salting-out) or removed (coprecipitation), more alternatives need to be considered. In Figure 3b the relative composition is represented by the solventing-out/coprecipitation rays that pass through points H and C. Figure 3c shows the relative composition diagram for this case. Based on Figure 3c, it is possible to construct Table 2, and then to construct the network for this system with salt 3 as a pseudosolvent.

The information in Table 2 can be used to construct the network of Figure 4. Nodes C and H are the operation points that can produce salt 2, salt 2 + salt 3, salt 1, and salt 1 + salt 3. Water can be added (a dilution or leaching step) or removed (an evaporation step). Salt 3, the pseudosolvent, can be added (a salting-out step) or removed (a coprecipitation step). In this figure, the open arrows represent the numerous feasible interconnecting paths that have been omitted for clarity.

For any quaternary system there are three possible partial cycles like the one shown in Figure 3, depending on which salt is considered to be the pseudosolvent. A network can be constructed for each partial cycle. Because these networks separate the quaternary mixture into single salts and two-solute systems (ternary systems), it is necessary to construct a network for each possible ternary system. An overall network can be constructed by combining these networks.

Usually a crystallizer is operated as close as practical to multiple saturation point to maximize product recovery; how-

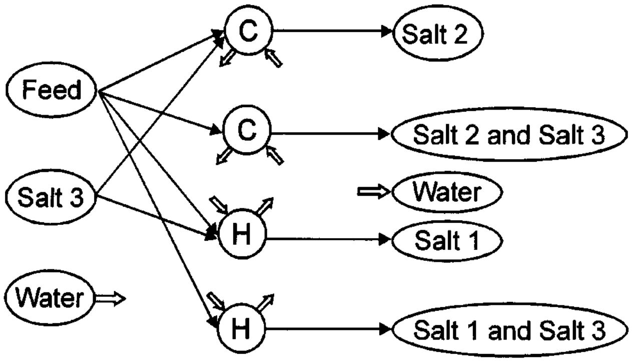

Figure 4. Network structure for the separation of salt 1 and salt 2 using salt 3 as pseudosolvent.

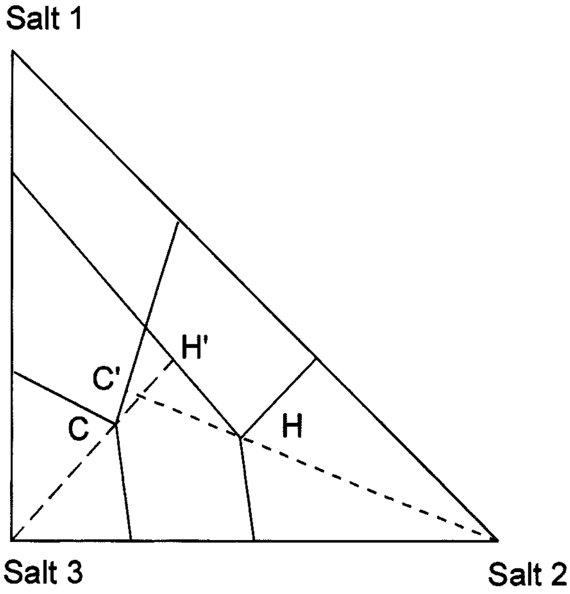

Figure 5. Alternative operation points.

ever, in systems with three or more solutes this can mean coprecipitating two or more salts. Therefore, other saturated solutions can be added to the set of potential operation points. For example, in Figure 5 points C' and H' can be added as potential operation points to the points H and C. It is also possible to eliminate schemes where valuable salts are used to salt out salts of little value merely by eliminating salting-out nodes.

Anhydrous or hydrated multiple salts

Formation of multiple salts is a common characteristic of inorganic systems. These multiple salts can be thought of as intermediate products that need further processing. Such processing can be easily included in the network representation. This is explained by Example 2, which includes several double salts.

Mathematical Formulation

Now that we have derived the network for the separation problem, we present the nonlinear programming formulation for the optimum selection of the separation sequence. To derive the mathematical formulation of the NLP problem, the following sets are defined to characterize the topology of the network. First, the set of nodes is defined as:

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

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

$$L_N = \{l | l \in L, \text{ with composition specified}\}$$

$$L_{UN} = \{l | l \in L, \text{ with composition not specified}\}$$

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

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

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

$$S_S = \{s | s \in S, \text{ intermediate solute product with unknown composition}\}$$

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

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

$$S_N^{\text{in}}(s) = S^{\text{in}}(s) \cap L_N$$

$$S_N^{\text{out}}(s) = S^{\text{out}}(s) \cap L_N$$

$$S_{UN}^{\text{in}}(s) = S^{\text{in}}(s) \cap L_{UN}$$

$$S_{UN}^{\text{out}}(s) = S^{\text{out}}(s) \cap L_{UN}$$

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

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

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

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

Each stream l is associated with the variable mass flow rate w_l and with the composition of each component. If the composition of component i of stream l is known, then it is represented by the parameter $x_{l,i}$. If the composition of component i of stream l is unknown, then it is represented by the variable $z_{l,i}$.

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

- Mass balances for operation point nodes:

$$\sum_{l \in S^{\text{in}}(s)} w_l - \sum_{l \in S^{\text{out}}(s)} w_l = 0 \qquad s \in S_M. \tag{1}$$

- Mass balance for each component in operation point nodes:

$$\sum_{l \in S_N^{\text{in}}(s)} w_l \cdot x_{l,i} + \sum_{l \in S_{UN}^{\text{in}}(s)} w_l \cdot z_{l,i} - \sum_{l \in S_N^{\text{out}}(s)} w_l \cdot x_{l,i} - \sum_{l \in S_{UN}^{\text{out}}(s)} w_l \cdot z_{l,i} = 0 \quad s \in S_M, \quad i \in I. \tag{2}$$

- Specification for feeds flow rates:

$$\sum_{l \in F(s)} w_l \cdot x_{l,i} = C_{s,i}^F \qquad s \in S_F, \quad i \in I_F(s), \tag{3}$$

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

- Specification for product flow rates:

$$\sum_{l\in P(s)} w_l \cdot x_{l,i} = C^P_{s,i} \qquad s\in S_P,\quad i\in I_P(s), \tag{4}$$

where $C^P_{s,i}$ is the desired quantity of component i in the final product s.

- Equality of composition for the inlet and outlet streams of the intermediate product nodes with unknown composition:

$$z_{l,i} = z_{m,i} \qquad l\in S^{\text{in}}_{UN}(s),\quad m\in S^{\text{out}}_{UN}(s),\quad s\in S_S. \tag{5}$$

- Nonnegativity and composition constraints:

$$1 \geq z_{l,i} \geq 0 \qquad w_l \geq 0 \tag{6}$$

The objective function minimizes the venture cost. The following equation can be used as an objective function,

$$\min_{w_l,\, z_{l,i}} \; \sum_{s\in S_M} C_s \cdot \left[\sum_{l\in S^{\text{in}}(s)} w_l \right]^{\alpha} + \sum_{s\in S_F} C_s \cdot \left[\sum_{l\in F(s)} w_l \right] + \sum_{s\in S_P} C_s \cdot \left[\sum_{l\in P(s)} w_l \right], \tag{7}$$

where C_s is the weighted cost coefficient. The first term on the lefthand side of Eq. 7 represents the annual capital cost, and the second and third terms represent the annual operation cost of raw material and products, respectively. Product costs count for solvent evaporation and residue loss. For the purposes of this study, all the C_s are equal to 1 and $\alpha = 1$.

Thus, the objective function in Eq. 7, subject to constraints in Eqs. 1 to 6, defines a nonlinear programming problem in which the variables to be optimized are mass flow rates w_l and the compositions $z_{l,i}$. The numerical solution to the NLP problem can be obtained with standard algorithms. In this work MINOS was used. The optimal solution of this NLP problem provides the separation system that can transform the multicomponent feed streams into the desired products.

An important question that arises on the validity of the proposed NLP formulation is whether a practical separation configuration can result from the imposed network. As was indicated by Floudas (1987), the recycle streams tend to take values of zero for the flow rates, which means that relatively simple separation sequence structures are to be expected when this approach is used.

Examples

In order to illustrate the procedure, three examples will be considered.

Example 1: Potash production

This example considers the production of potassium chloride from 100 units of sylvinite (47.7% KCl, 52.3% NaCl). This example was studied by Cisternas and Rudd (1993), Rajagopal et al. (1988), and Cisternas and Swaney (1998). This small problem was selected to explain the synthesis approach. Data on phase equilibrium for the system KCl–NaCl–H_2O from Linke and Seidell (1965) and the relative composition are given in Table 3. KCl was chosen to be salt 1 and NaCl to be salt 2, but this selection in no way restricts our analysis, and the same results would be obtained if NaCl were chosen as salt 1.

Table 3. Data for Example 1

Key	Temp. °C	Saturated Solution, wt. % KCl	NaCl	H_2O	Solid Phases	R
C	30	11.7	20.25	68.05	KCl + NaCl	0.58
H	100	22.20	15.90	61.9	KCl + NaCl	1.40

The full network can be easily generated using the relative composition diagram in Figure 6a. The feasible operations consist of:

(1) Point H can be used to precipitate NaCl, starting with the saturated solution C. This is clear because H is in equilibrium with NaCl, and the relative composition of point C, R^C, is between R^H and R^{NaCl}.

(2) Point C can be used to precipitate KCl, starting with the saturated solution H. Note that in this case C is in equilibrium with KCl, and the relative composition of point H is between R^C and R^{KCl}.

(3) Feed can be added to operation points H and C.

(4) Water can be added or removed from points H and C.

The network structure in Figure 6b employs seven nodes and ten arcs. Node 1 is the sylvinite feed node, which can be added to nodes 3 and 4. Nodes 3 and 4 correspond to the multiple saturation points at the hot and cold temperatures,

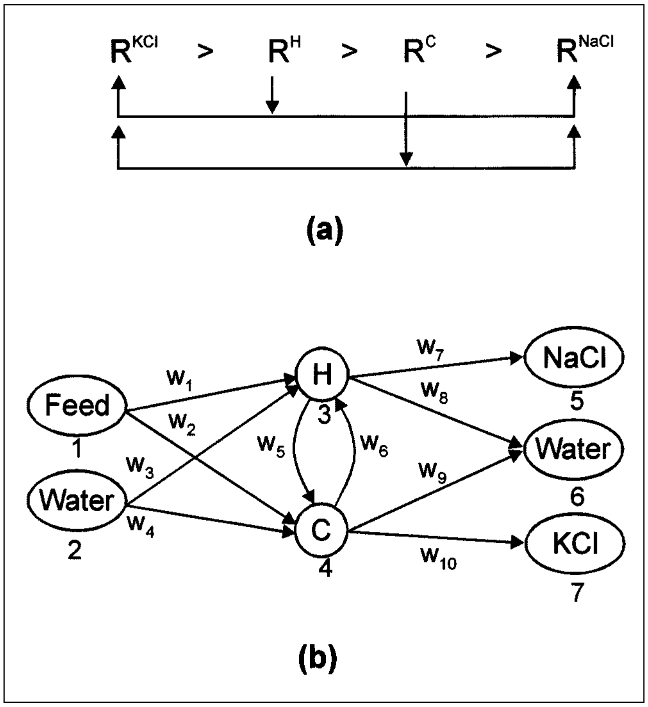

Figure 6. Relative composition diagram and network structure for Example 1.

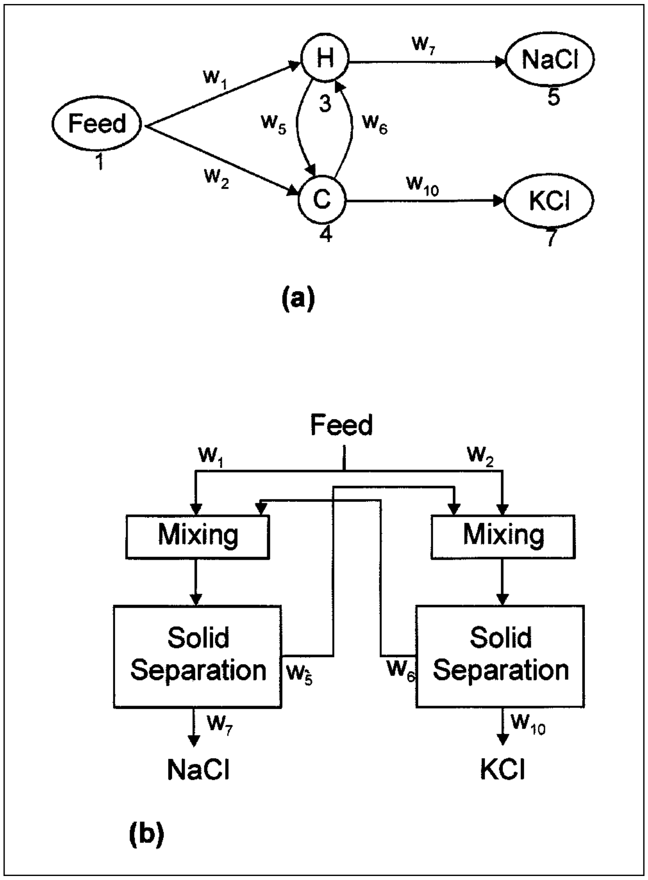

Figure 7. Solution flow and corresponding flow sheet for Example 1.

respectively. Node 3 allows the separation of NaCl, whereas node 4 allows the separation of KCl. Nodes 5 to 7 are product nodes. The allowed streams are also shown in Figure 6b. For example, w_3 represents the mass flow rates from node 2 to node 3.

For this example, the mathematics model corresponds to a linear programming problem because the only variables are the flow rates. All the compositions are known.

The solution to this example corresponds to the following flow rates: $w_1 = 83.413$, $w_2 = 16.587$, $w_5 = 344.264$, $w_6 = 313.151$, $w_7 = 52.3$, $w_{10} = 47.7$. Figure 7 shows the network solution and the flow-sheet structure corresponding to the solution. The solution found is the same as that found by Cisternas and Swaney (1998), where the sylvinite was divided into two parts. Cisternas and Swaney used a nine-node network and 48 single variables, whereas in this work a seven-node network and eleven single variables were used. This allows reduction of the execution time by over 90% using GAMS/MINOS.

In this case, the reduction in the execution time is not important, because this is a very small problem. However, using the relative composition diagram allows the operation nodes (multiple saturation nodes) to be reduced from four to two. As a result, the three flow-sheet alternatives can be examined from the network in Figure 6b. Therefore, the relative composition diagram can be used to study flowsheet alternatives without it being necessary to optimize the small problems.

Table 4. Data for Example 2

Key	Temp. °C	Saturated Solution, wt. %			Solid Phase
		$MgSO_4$	Na_2SO_4	H_2O	
C	18.7	20.57	11.8	67.63	$Mg_7 + Na_{10}$
*D*1	25	21.15	13.0	65.85	$Mg_7 + DS1$
*D*2	25	16.6	17.8	65.6	$DS1 + Na_{10}$
*E*1	50	31.32	4.74	63.94	$Mg_6 + DS1$
*E*2	50	11.98	23.25	64.77	$DS1 + Na$
*F*1	97	32.2	5.55	62.25	$Mg_1 + DS2$
*F*2	97	14.4	19.15	66.45	$DS2 + DS3$
*F*3	97	5.88	26.9	67.22	$DS3 + Na$

$Mg_7 = MgSO_4 \cdot 7H_2O$; $Mg_6 = MgSO_4 \cdot 6H_2O$; $Mg_1 = MgSO_4 \cdot H_2O$
$Na_{10} = Na_2SO_4 \cdot 10H_2O$; $Na = Na_2SO_4$
$DS1 = MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$
$DS2 = MgSO_4 \cdot Na_2SO_4$
$DS3 = MgSO_4 \cdot 3Na_2SO_4$

Example 2: Separation of magnesium sulfate and sodium sulfate from astrakanite

This example was presented by Cisternas and Swaney (1998). The problem consists of separating magnesium sulfate and sodium sulfate from 100 units of the double salt astrakanite, $MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$. Equilibrium data from Linke and Seidell (1965) are shown in Table 4. This system presents several temperature regions: first, double salt will not form at low temperatures; then there is a region where one double salt will form; and at high temperatures two double salts will form. Figure 8 shows the phase diagram of this system. The design of alternative process flow sheets for this system is complex if two temperatures are considered as operation points, but it is even more difficult if more than two temperatures are considered, because the phase diagram will become more complex, and there will be many alternative process flow sheets.

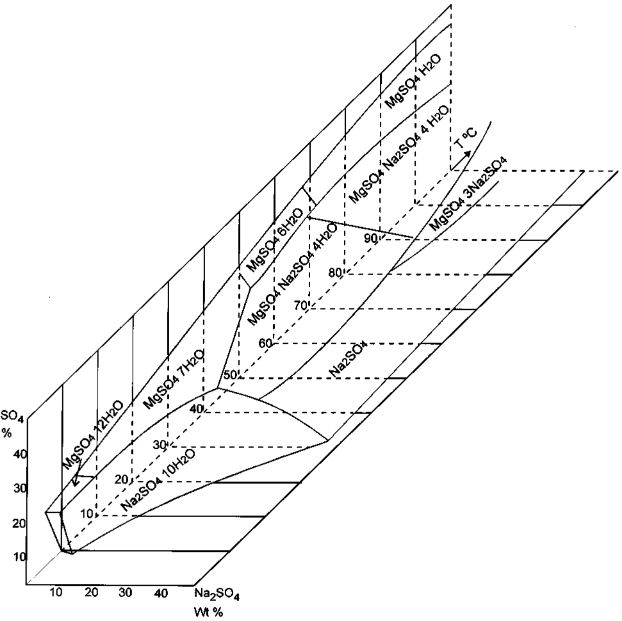

Figure 8. Phase diagram for the $MgSO_4$–Na_2SO_4–H_2O system.

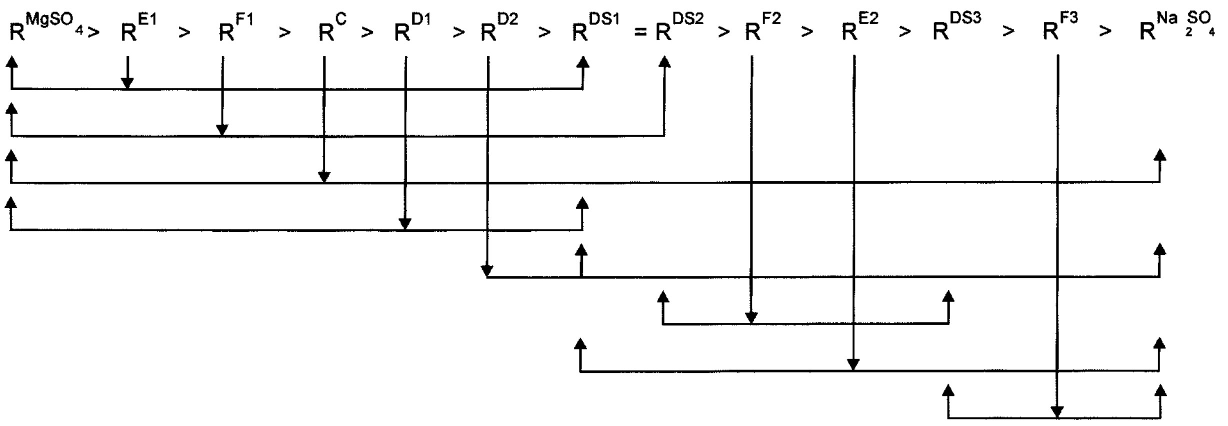

Figure 9. Relative composition diagram for Example 2.

The full network can be easily generated using the relative composition diagram in Figure 9. In this case, magnesium sulfate was chosen to be salt 1, and sodium sulfate was chosen to be salt 2. There are three intermediate products: DS1, DS2, and DS3. The double salt 1 and double salt 2 have the same relative composition. From Figure 9 it is clear that $E1$ cannot be used to precipitate $MgSO_4$, $D2$ cannot be used to precipitate DS1, $F2$ cannot be used to precipitate DS2, and $F3$ cannot be used to precipitate DS3 and Na_2SO_4. Then, the feasible operations consist of:

(1) Point $E1$ can be used to precipitate DS1, starting with saturated solutions $F1$, C, $D1$, and $D2$. This is clear because $E1$ is in equilibrium with DS1 and the relative composition of points $F1$, C, $D1$, and $D2$ are between R^{E1} and R^{DS1}.

2. Point $F1$ can be used to precipitate $MgSO_4$, starting with the saturated solution $E1$, and can be used to precipitate DS2, starting with saturated solutions C, $D1$, and $D2$.

3. Point C can be used to precipitate $MgSO_4$, starting with saturated solutions $E1$ and $F1$. Also, point C can be used to precipitate Na_2SO_4, starting with saturated solutions $D1$, $D2$, $F2$, $E2$, and with intermediate products DS1, DS2, and DS3.

4. Point $D1$ can be used to precipitate $MgSO_4$, starting with saturated solutions $E1$, $F1$, and C. Also, it can be used to precipitate DS1, starting with the saturated solution $D2$.

5. Point $D2$ can be used to precipitate Na_2SO_4, starting with saturated solutions $F2$, $E2$, and with intermediate product DS3.

6. Point $F2$ can be used to precipitate DS3, starting with the saturated solution $E2$.

7. Point $E2$ can be used to precipitate DS1, starting with the saturated solution $F2$, and it can be used to precipitate Na_2SO_4, starting with the intermediate product DS3.

8. Feed can be added to the operation points C, $D1$, $D2$, $E1$, $E2$, $F1$, and $F2$.

9. Water can be added or removed from points C, $D1$, $D2$, $E1$, $E2$, $F1$, and $F2$.

The network structure in Figure 10 employs 19 nodes and 83 arcs. In the figure, the open arrows represent the feasible interconnecting paths that have been omitted for clarity. Node 1 is the astrakanite feed node, which can be added to nodes 3–13. These nodes correspond to the multiple saturation points, while nodes 14, 15, and 16 correspond to intermediate products, and nodes 17–19 are product nodes. The allowed streams are also shown in Figure 10.

For this example, the mathematical model corresponds to a linear programming problem, because all the compositions are known. Thus, the only variables are the flow rates.

The solution to this example corresponds to the following nonzero flow rates: $w_5 = 100.000$, $w_{16} = 242.316$, $w_{25} = 340.662$, $w_{26} = 55.600$, $w_{41} = 94.651$, $w_{46} = 152.488$, $w_{59} = 94.651$, $w_{63} = 96.304$, $w_{64} = 73.680$, $w_{70} = 149.123$, $w_{75} = 23.209$. Figure 11a shows the network solution, and Figure 11b shows the structure corresponding to the solution. This example demonstrates the ability of the network flow method

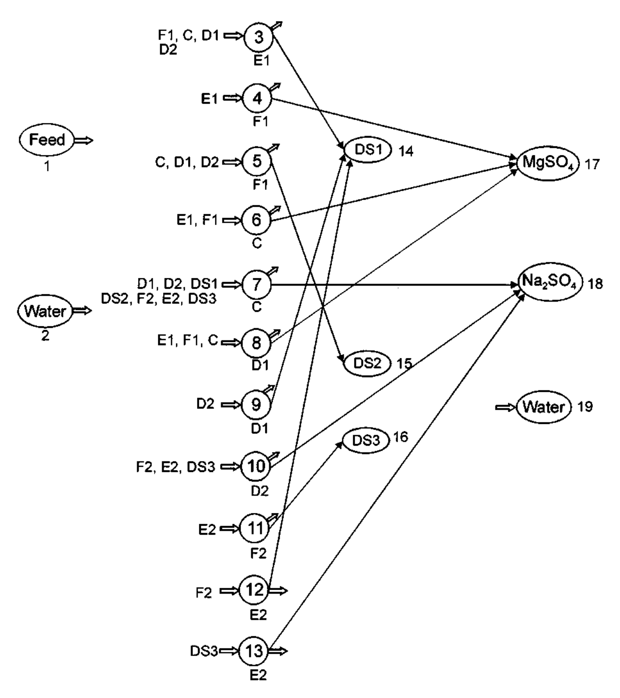

Figure 10. Network structure for Example 2.

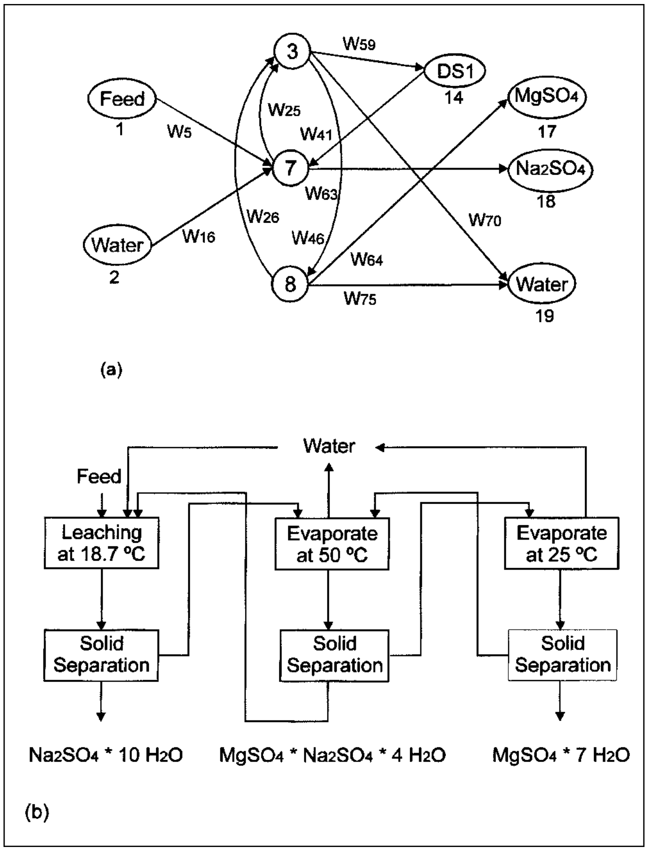

Figure 11. Solution flow and corresponding flow sheet for Example 2.

to choose from among several alternate temperatures. In this case, the optimal solution considers the operation at three temperatures.

The solution found is the same as that found by Cisternas and Swaney (1998), where the astrakanite is leached at 18.7°C. Cisternas and Swaney used a 24-node network and 908 single variables, while we used a 19-node network and 83 single variables in this work. Also the Cisternas and Swaney model uses over 1000 single equations, while this work uses 60 equations. This allows a reduction in execution time by 90% using GAMS/MINOS.

The solution includes two evaporation steps and one dilution step. The astrakanite is leached at 18.7°C, leaving the sodium sulfate precipitated. Magnesium sulfate is crystallized by cooling and evaporating at 25°C. Only one of the three double salts, astrakanite, is used in the flow sheet. Astrakanite is precipitated by evaporation at 50°C.

Example 3: Production of potassium salts

We seek to separate an aqueous solution of 11.5% KCl, 19.8% KNO_3, 3.3% K_2SO_4, and 65.4% water. Equilibrium data from Linke and Seidell (1965) are shown in Table 5. Points $C1$ and $H1$ correspond to multiple saturation points of the quaternary system $KCl-KNO_3-K_2SO_4$-water, where as points $C2-C4$ and $H2-H4$ correspond to multiple saturation points of the ternary systems. This example was selected to illustrate application of the method to multicomponent systems.

Table 5. Solubility Data for the System $KCl+KNO_3+K_2SO_4+H_2O$

Key	T (°C)	g/100 g of Saturated Solution KCl	KNO_3	K_2SO_4	Solid Phase
$C1$	25	21.6	14.6	0.9	$KCl+KNO_3+K_2SO_4$
$C2$		0.0	25.4	4.0	$KNO_3+K_2SO_4$
$C3$		26.0	0.0	1.1	$KCl+K_2SO_4$
$C4$		21.9	14.6	0.0	$KCl+KNO_3$
$H1$	75	15.6	43.9	0.7	$KCl+KNO_3+K_2SO_4$
$H2$		0.0	59.3	1.3	$KNO_3+K_2SO_4$
$H3$		32.3	0.0	1.4	$KCl+K_2SO_4$
$H4$		15.5	46.3	0.0	$KCl+KNO_3$

Source: Linke and Seidell (1965).

The approach to solving this problem is similar to those previously used for ternary systems, only more variations are possible. First, a network is constructed for each salt as pseu-

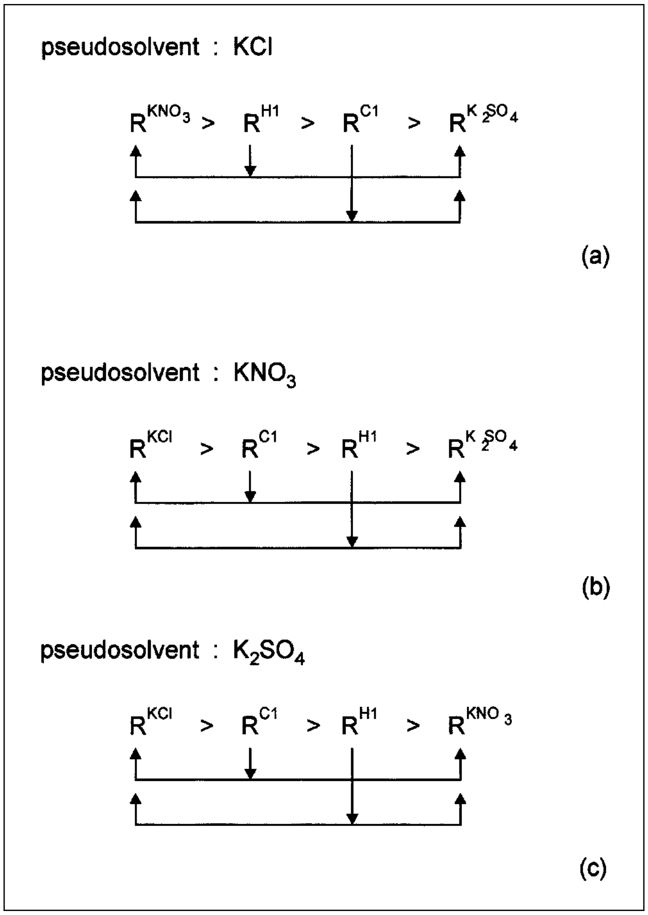

Figure 12. Relative composition diagrams for Example 3.

(a) KCl as pseudosolvent. (b) KNO_3 as pseudosolvent. (c) K_2SO_4 as pseudosolvent.

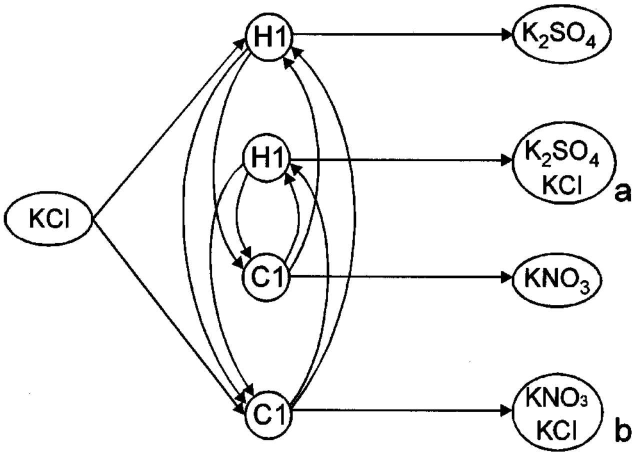

Figure 13. Network structure for relative composition diagram in Figure 12a.

dosolvent for the quaternary system. Three relative composition diagrams are constructed, as in Figure 12. One salt is considered to be the pseudosolvent, and relative compositions are calculated using the other two salts. A network is constructed for each relative composition diagram. For example, Figure 13 shows the network for the relative composition diagram of Figure 12a. In this case, point $H1$ can be used to precipitate K_2SO_4, but since KCl can be added (salting-out) or removed (coprecipitation), two nodes need to be considered. In the same way, point $C1$ can be used to salt-out KNO_3 or to coprecipitate KNO_3 and KCl. Nodes *a* and *b* in Figure 13 correspond to intermediate products where the compositions are unknown.

Second, relative composition diagrams and networks are constructed for each ternary system. These networks are used to allow the processing of intermediate products.

Third, the full network can be easily generated as the aggregate of all networks. Figure 14 shows the overall network for the example. The network structure employs 28 nodes and 126 arcs. Node 1 is the aqueous-solution feed node, which can be added to nodes 6–15. Nodes 3–5 are salt feeds to allow salting-out operations. Nodes 6–15 correspond to the multiple saturation points for the quaternary system, and nodes 19–24 correspond to the multiple saturation points for the ternary system. Nodes 16–18 are intermediate products, and nodes 25–28 are product nodes. For simplicity, only some of the allowed streams are shown in Figure 14.

For this example, the mathematics model corresponds to a nonlinear programming problem, because the compositions of the input and output streams to and from nodes 16–18 are unknown. All the other compositions are known. This problem has 155 single equations and 167 single variables. The problem was solved with MINOS 5.3 using GAMS on a PC.

Figure 15 shows the network solution, and Figure 16 shows the flow-sheet structure corresponding to this solution. This solution corresponds to the same kind of solution that can be found with the Cisternas and Rudd (1993) method, except that the intermediate product of node 16 is divided into two to feed nodes 19 and 20. However, this does not mean that the only feasible solution is composed of simple cycles, because multiple coupled cycles are allowed in the overall network.

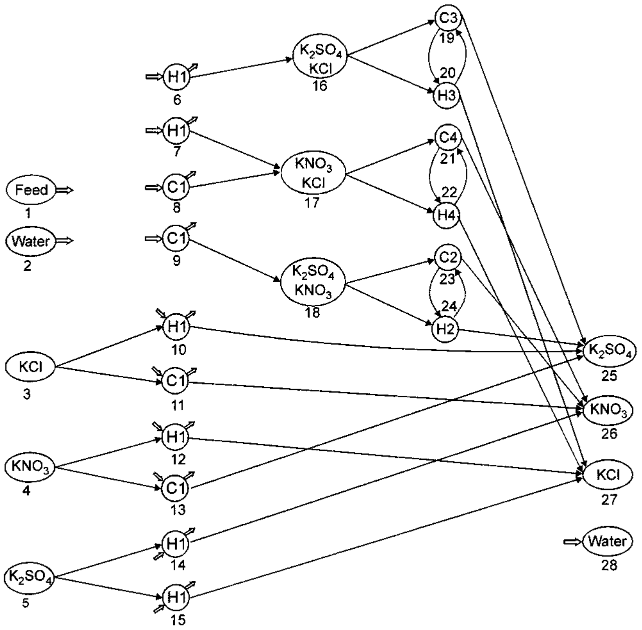

Figure 14. Overall network structure for Example 3.

Conclusions

The synthesis problem of separating one or several multicomponent streams into several multicomponent or pure-product streams by fractional crystallization has been considered. The synthesis approach proposed is based upon a flow network superstructure that has embedded streams between several key states. Optimizing this network through a nonlinear programming formulation, solution networks are derived that can be transformed to feasible flow sheets.

The construction of the network is accomplished by selecting appropriate equilibrium points at several temperatures. The relative composition diagram is used to screen feasible nodes, which allows a decrease in the number of nodes in the network, and consequently the number of equations and variables in the mathematical model.

The principal advantages of the method presented are (1) the ability to handle systems with three or more solutes; (2)

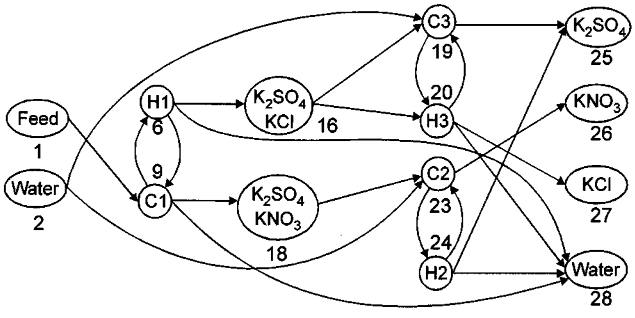

Figure 15. Solution flow for Example 3.

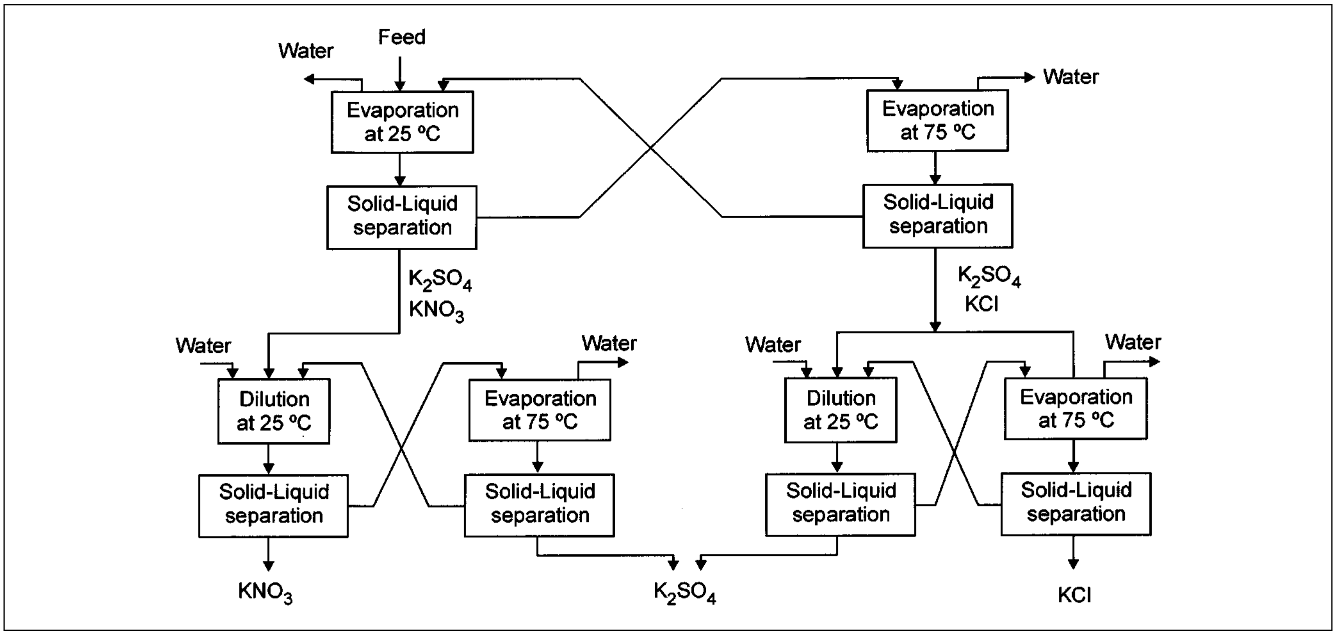

Figure 16. Corresponding flow sheet of solution flow of Figure 15.

the ability to handle several temperatures as potential operation conditions; (3) the ability to handle systems by the formation of double salts; (4) the possibility of considering several feeds and products; and (5) consideration of the general process flow patterns.

Acknowledgment

The author acknowledges the financial support of the CONICYT for a grant (FONDECYT 1961270) in support of work of which this research was a part.

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Manuscript received Oct. 16, 1998, and revision received Mar. 17, 1999.