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REPRESENTATION OF MATERIAL BALANCE FOR FRACTIONAL CRYSTALLIZATION OF RECIPROCAL SALT PAIR SYSTEMS: KNO_3 PRODUCTION CASE STUDY

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Abstract: In this paper, determination of material balance for reciprocal salt pair systems is considered and special case of KNO_3 production is solved. A scheme is presented for calculation of material balance which is based on the conservation of ions and water. Material balance requires equilibrium composition and phase diagram of solid-liquid equilibria that is calculated by extended UNIQUAC thermodynamic model.

Keywords: *Fractional crystallization, KNO_3 production, material balance, reciprocal Salt Pair systems*

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1. Introduction

Fractional crystallization is a separation technique employed to produce a wide variety of materials, including production of potassium nitrate, potassium chloride, potassium sulfate, sodium sulfate, boric acid, adipic acid. The technique consists of sequences of heating, cooling, evaporation, dilution, solventing-out, salting-out, and solid-liquid separation. Fractional crystallization effects separations by manipulating the relative solubilities of the components in a solution by dilution, evaporation, dissolution, stream combination and temperature change.

Many articles have been published concerning the synthesis of separation processes to obtain salts from mixtures of salts. These studies can be classified into two categories: those that use a phase diagram to identify the types of processes that may be applied to specific types of solid-liquid equilibrium behavior [1–4], and those that use a network flow model between a priori determined thermodynamic states that allow selection of an optimal structure [5–7].

When two salts have no ions in common, a double decomposition can occur in which a pair of salts is reconstituted into another pair. This phenomenon is known as reciprocal salt pairing, or metathetical salt systems. This type of system is of interest for the production of various chemical compounds, for example, the production of potassium nitrate beginning with sodium nitrate and potassium chloride. Purdon and Slator's book [8] describes precisely how to present such phase equilibrium data in a diagram. These authors also explained how to present evaporation paths by means of phase diagrams. A simple description can be found in Mullin's book [9]. Fitch [10] discussed how the phase diagram could be used to represent processes for fractional crystallization, including the treatment of reciprocal salt pairs. However, he did not address the problem of synthesizing the process flowsheet. Ng [1] presents a synthesis method for separation of solids based on selective crystallization and dissolution. The method can be applied to mixtures of solids that do not form double salts and have solubilities that are monotonically increasing or decreasing functions of temperature. Cisternas and Rudd [2] presented a systematic procedure for identification of alternative process designs for fractional crystallization from solution. They searched designs that involve low rates of recycle, evaporation, and dilution. Dey and Ng [3] present guideline for the design of fractional crystallization processes to separate two- and three-solute mixtures. By using solvent addition/removal, stream combination and cooling/heating these processes bypass regions of multiple saturation in the phase diagram and recover solute. Design equations are formulated and the constraints on the design variables are identified. Effect of changes in the design variables on recycle flows is discussed and the cost of fractional crystallization separation is estimated.

Berry and Ng [4] gave a method for the separation of salts in the pure, solid state for reciprocal salt pair systems. They identified three classes of separations that could be used to separate simple salts from a solution. These separation classes could be used as guidelines for the conceptual design of separation processes for these systems. However, this procedure is limited, as it is common that metathetical salt systems can have complex behaviors that do not compare with the examples studied by Berry and Ng, or specific problem conditions may apply, such as the existence of more than one feed. Also, certain flow pattern alternatives, such as stream splitting or mixing, may be difficult to envision within the phase diagram. Cisternas and Swaney [5] presented a method to synthesize process flow sheets for separations of mixtures by fractional crystallization. Using equilibrium data for a candidate set of potential operating point temperatures, a network flow model is constructed to represent the set of potential separation flow sheet structures that can result. By employing specified approaches to multiple saturation point conditions, linear network constraints are obtained. Solution of the network flow model shows the

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optimal mass flow pattern between the candidate equilibrium states and from this the corresponding process flow sheet is deduced. The method as presented is generally applicable to problems with two salts and one or more solvents, including systems forming one or more multiple salts or hydrates. Then, Cisternas [6] presented network flow model for synthesizing crystallization-based separations for multicomponent systems. The construction of the network flow is based on the identification of feasible thermodynamic states. In other words, 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 method allows consideration of several operation temperatures, complex solid-liquid equilibrium behavior, and several multi component 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.

Cisternas et al. [7] presented a methodology 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 flow sheet 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 modeled 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 transhipment problem.

Improving the recovery of the adipic acid in an existing fractional crystallization process is considered by Cesar and Ng [11]. Solid-liquid phase behaviors and techniques relevant to product recovery are discussed. Retrofit targets are identified through an analysis of the phase diagram of the mixture under consideration. Conceptual design techniques consisting of heat and mass balances, heuristics, and shortcut unit models are used to determine the necessary changes in flow sheet structure and equipment design in order to meet the retrofit objective. In another study, Thomsen et al. [12] simulated and optimized fractional crystallization processes, including reciprocal salt pairs. The analysis of alternatives that can be obtained by simulation is limited, however, because a very large number of processing possibilities exists. Cisternas et al. [13] present a method for the design of separation schemes based on fractional crystallization for systems formed of reciprocal salt pairs. The method is based on a network model with flows between thermodynamic states. Using the phase diagram, a method is developed for identification of a set of solid-liquid equilibrium points that are believed to include the best prospects for operating points. Then, based on these points, only the feasible physical interconnections are identified, in order to reduce the number of arcs in the flow network. A mathematical model is developed based on the network flow model to find the optimal flow pattern for the separation of the reciprocal salt pairs. A method for determining the desired process flow sheet for fractional crystallization processes is presented by Cisternas et al. [14] 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 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 is shown. Previous studies present either process design for fractional crystallization or calculation of material balance by mathematical programming and a convenient way and detailed presentation of material balance is not presented.

In this paper a convenient method for material balance calculation of reciprocal salt pairs is introduced. All streams in the process are mixtures of ions in water because all salts decompose in water completely. By this method, we obtain ionic balance in process equipment. The resulting ionic flow rates are transformed to flow rates of salts which are reported as results of material balance.

2. Description of Process Studied

A reciprocal salt pair is formed by dissolving two salts that do not have common ions in a solvent. Through a metathesis reaction, a total of four simple salts may precipitate from this solution which is a mixture of ions in solution. For example, in the reaction between NaNO3 and KCl, KNO3 and NaCl can be produced by the following reaction:

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3$$

Quaternary ionic solutions with two anions and two cations can be represented in a three dimensional diagram with the anion charge fraction as the x-coordinate, the cations charge fraction as the y-coordinate and the mole ratio of water as the z-coordinate. The system can also be represented on a water-free basis as a two-dimensional diagram named Janecke projection. The quaternary diagram represents mole compositions of different solutions on a dry basis. For the system (Na^+, K^+, Cl^-, NO_3^-) in water the definitions are (n is number of moles):

$$x - \text{coordinate} = \frac{n_{NO_3^-}}{n_{Cl^-} + n_{NO_3^-}} \tag{1}$$

$$y - \text{coordinate} = \frac{n_{K^+}}{n_{Na^+} + n_{K^+}} \tag{2}$$

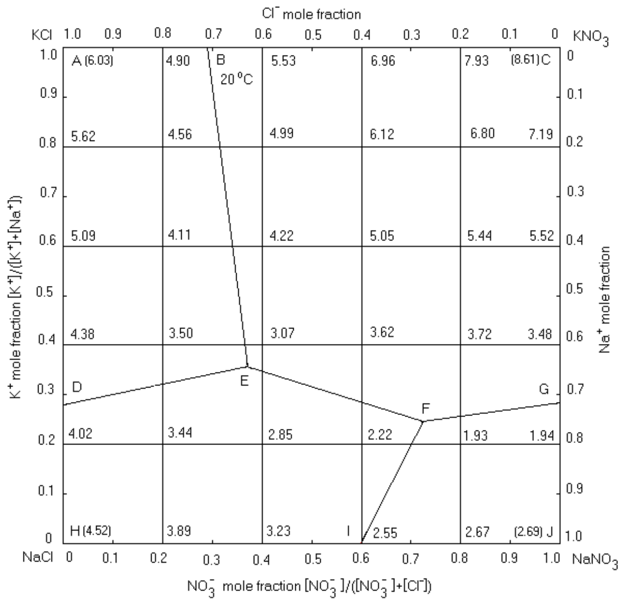

Figure 1: Phase diagram of system (K^+, Na^+, Cl^-, NO_3^-)-H_2O at 20°C calculated by extended UNIQUAC model. Numbers on intersections and four corners represent moles of H_2O/total moles of ions

$$z-\text{coordinate} = \frac{n_{H_2O}}{n_{Na^+} + n_{K^+} + n_{Cl^-} + n_{NO_3^-} + n_{H_2O}} \tag{3}$$

In the Janecke projection z-coordinate is depicted in separate diagram [9].

The phase diagram may be considered as visual tool which can be employed to design fractional crystallization processes, for example, information on which salt can be encountered in a given solution as a function of temperature as well as to display the process paths for such processes.

Figure 1 shows the Janecke projection of phase diagram representing an aqueous system formed by monovalent salts K^+, Na^+, Cl^-, NO_3^- and H_2O at 20°C. The coordinates of one point in the diagram are given by the ratio of the concentration of K^+ to the total cations concentration (K^+ + na^+), the ratio of the concentration of NO_3^- to total concentration of anions (Cl^-+NO_3^-), and by the moles of solvent per total moles of ions. Numbers on intersections and four corners of Figure 1 represent moles of H_2O/total moles of ions at equilibrium points calculated by extended UNIQUAC model. The points A, C, H and J are the saturated solutions of pure salts dissolved in water. The double saturation points (B, D, G, I) represent solutions saturated with two salts. Points E and F represent triple saturation points of the quaternary system. At a given temperature, the double saturation lines divide the Janecke projection in four single saturation regions, one for each component. Regions formed by the ABED, BCGFE, DEFIH and FGJI borders represent saturation surfaces of the KCl, KNO_3, NaCl and $NaNO_3$ salts, respectively. The IF, GF, DE, BE and EF borders represent conditions under which the solution is saturated by two salts. Not all the combinations are possible, and thus no conditions exist in the phase diagram of Figure 1 under which KCl and $NaNO_3$ can be co-crystallized. These two salts are termed incompatible salts, while the NaCl-KNO_3 pair, which co-crystallize at border EF, are termed compatible salts. Table 1 shows a few predictions of extended UNIQUAC model of saturation lines in Janecke projection at 20°C which are used in Figure 1.

Table 1: Some predictions of extended UNIQUAC model for saturation lines of Janecke projection at 20°C that are used in Figure 1

K^+	Na^+	Cl^-	NO_3^-	$\frac{\text{moles of } H_2O}{\text{total moles of ions}}$
NaCl-KNO_3 saturation line				
0.2459	0.7541	0.2737	0.7263	1.7252
0.2597	0.7403	0.3884	0.6116	2.0871
0.3060	0.6940	0.5397	0.4603	2.4581
0.3571	0.6429	0.6289	0.3711	2.6004
NaCl-KCl saturation line				
0.2805	0.7195	1.0000	0.0000	3.8108
0.2992	0.7008	0.8853	0.1147	3.4451
0.3300	0.6700	0.7334	0.2666	2.9500
0.3571	0.6429	0.6289	0.3711	2.6004
KCl-KNO_3 saturation line				
1.0000	0.0000	0.7105	0.2895	4.3998
0.7610	0.2390	0.7056	0.2944	3.9865
0.5241	0.4759	0.6813	0.3187	3.3426
0.3571	0.6429	0.6289	0.3711	2.6004
NaCl-$NaNO_3$ saturation line				
0.0000	1.0000	0.4013	0.5987	2.5526
0.0764	0.9236	0.3664	0.6334	2.3111
0.1774	0.8226	0.3139	0.6861	1.9700
0.2459	0.7541	0.2737	0.7263	1.7252
$NaNO_3$-KNO_3				
0.2834	0.7166	0.0000	1.0000	1.6250
0.2640	0.7360	0.1119	0.8881	1.7001
0.2531	0.7469	0.1953	0.8047	1.7267
0.2459	0.7541	0.2737	0.7263	1.7252

In the phase diagram as presented in Figure 1 more than one isotherm must be shown in order to design processes for separation by fractional crystallization. For this reason, it is more common to present this type of system by the Janecke projection. In addition to 20°C (Figure 1), the phase diagram at 100°C is also included in Figure 2. It is possible to design various processing alternatives between these two temperatures. Assume that the production of KNO_3 (and thus NaCl) is desired beginning with KCl and $NaNO_3$. By adding or removing water, any mixture of KCl and $NaNO_3$ can be brought to a position in the diagram, where only one salt precipitates. By regulating temperature and adding or evaporating water, a cycle for fractionating the two salts can be found. One possible process is indicated in Figure 2 by points O, K, L and M. Any mixture of KCl and $NaNO_3$ lies on the line connecting them. Process feed is formed by mixing equimolar mixture of KCl and $NaNO_3$ at point O. When mixing two streams represented by two different points in a quaternary diagram, the the resulting stream will have a composition lying on a line between the two points representing the streams. The feed is mixed with solution M, producing mixture K. The water quantity is adjusted to precipitate NaCl and generate solution L at 100 . The water quantity and temperature in mixture L is different from mixture M. The solution L is cooled and the water adjusted in order to crystallize KNO_3 and produce solution M, which is recycled to the process and mixed with feed. The solution from which crystallization takes place can be considered as a mixture of the solid phase and the liquid phase. Hence, the gross composition of the solution is on a straight line between the solid salt and the solubility curve corresponding to the salt. Note

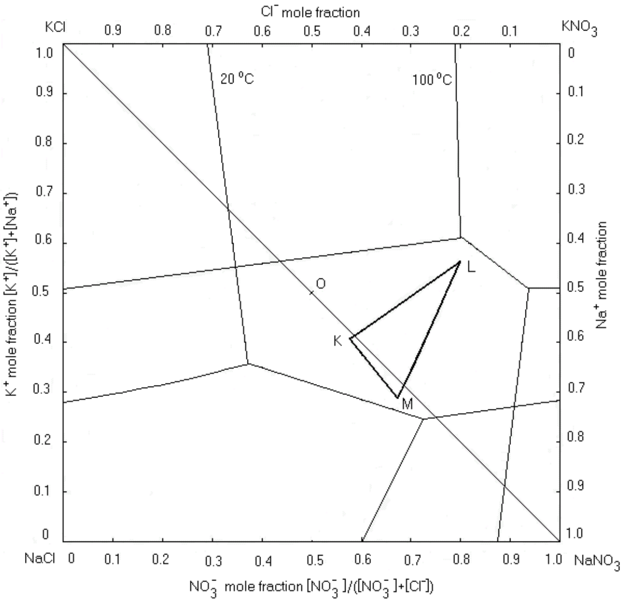

Figure 2: Two isotherms and cyclic process for fractional crystallization of NaCl (at 100°C) and KNO_3 (at 20°C)

that Janecke projection shows ionic composition of solution in equilibrium with salt. Solution L is in equilibrium with NaCl salt (at 100°) and solution M is in equilibrium with KNO_3 salt (at 20°). It is clear that more alternatives exist, but for our aim which is describing material balance in reciprocal salt pair system only one alternative (i.e. process OKLM in Figure 2) is sufficient. It should be noted that all solutions O, K, L, M are ionic mixture in water.

The problem to be solved can be defined in the following way: given the amount of desired product and the conditions of solid-liquid equilibrium at two temperatures, find the flow rate of salts and water in streams of the process. It is clear that the phase diagram at different temperatures must be available to calculate solid-liquid equilibrium.

3. Calculations of Phase Diagram by Extended UNIQUAC Model

Design of fractional crystallization processes requires a detailed knowledge of the phase equilibria for such systems. It is necessary to have phase diagram of system K^+, Na^+, Cl^-, NO_3^- in water at different temperatures. By use of the phase diagram, ionic composition and amount of water in solution which is in equilibrium with the crystallized salt can be calculated. The thermodynamic model used to compute phase equilibrium is the Extended UNIQUAC model described by Thomsen et al. [15] and applied for describing SLE, VLE and thermal properties of aqueous electrolyte systems. Extended UNIQUAC model comprises a Debye-Huckel term to describe the long range electrostatic forces and a UNIQUAC term to describe short range interactions. Hence, the excess Gibbs energy expression is represented by the sum of three terms: a combinatorial or entropic term and a residual or enthalpic term, as for nonelectrolyte systems (short-range contribution), and an electrostatic term (long-range contribution):

$$G^E = G^E_{SR} + G^E_{LR} = G^E_{\text{combinatorial}} + G^E_{\text{residual}} + G^E_{\text{Debye-Huckel}} \tag{4}$$

Table 2: Extended UNIQUAC r and q parameters [18]

	r_i	q_i
H_2O	0.9200	1.4000
Na^+	1.4034	1.1990
K^+	2.2304	2.4306
Cl^-	10.3860	10.1970
NO_3^-	5.4041	6.2074

Table 3: u^0_{ij} parameters for calculating extended UNIQUAC interaction energy parameters [18]

	H_2O	Na^+	K^+	Cl^-	NO_3^-
H_2O	0				
Na^+	733.286	0			
K^+	535.023	-46.194	0		
Cl^-	1523.39	1443.23	1465.18	2214.81	
NO_3^-	998.92	797.474	818.568	2175.02	2753.71

The combinatorial and the residual terms are identical to those used in the traditional UNIQUAC equation. The interaction parameters are considered temperature dependent:

$$u_{kl} = u^0_{kl} + u^t_{kl}(T - 298.15) \tag{5}$$

which is also used in the case $k = l$. The only parameters for the Extended UNIQUAC model are the UNIQUAC interaction parameters and the volume and surface area parameters. More information can be found in the literature [15–17]. Extended UNIQUAC volume and surface area parameters and interaction parameters are reported in Table 2, 3 and 4 [18].

The equilibrium between an aqueous phase and the solid salt consisting of κ cations K, α anions A, and n water molecules can be described by the equation:

$$K_\kappa A_\alpha \cdot n\mathrm{H_2O}(s) \leftrightarrow \kappa K(aq) + \alpha A(aq) + n\mathrm{H_2O} \tag{6}$$

At equilibrium, the chemical potential (μ) of the solid salt is equal to the sum of the chemical potentials of the salt's constituent parts. The condition for equilibrium therefore is:

$$\mu_{K_\kappa A_\alpha n\mathrm{H_2O}(s)} = \kappa\mu_K + \alpha\mu_A + n\mu_{\mathrm{H_2O}} \tag{7}$$

The chemical potential of component i is:

$$\mu_i = \mu_i^0 + RT\ln(a_i) \tag{8}$$

Table 4: u^t_{ij} parameters for calculating extended UNIQUAC interaction energy parameters [18]

	H_2O	Na^+	K^+	Cl^-	NO_3^-
H_2O	0				
Na^+	0.4872	0			
K^+	0.9936	0.119	0		
Cl^-	14.631	15.635	15.329	14.436	
NO_3^-	9.3251	9.3047	10.302	13.449	2.2866

Table 5: Coordinates of chosen points K, L and M in Janecke projection to calculate material balance and ratio of moles of water to total moles of ions

Solution	K^+(%)	Na^+(%)	Cl^-(%)	NO_3^-(%)	$\frac{\text{moles of } H_2O}{\text{total moles of ions}}$
K	44.0171	55.9827	55.9827	44.0171	1.9916
L	57.3281	42.6717	42.6717	57.3281	1.5563
M	38.8164	61.1835	61.1835	38.8164	2.9329

Table 6: Mole fraction of ions and water in points K, L and M calculated by data in Table 5

Solution	x_{K^+} (%)	x_{Na^+} (%)	x_{Cl^-} (%)	$x_{NO_3^-}$ (%)	x_{H_2O} (%)
K	7.3567	9.3565	9.3565	7.3567	66.5734
L	11.2129	8.3462	8.3462	11.2129	60.8815
M	4.9347	7.7783	7.7783	4.9347	74.5739

where, μ_i^0 is the chemical potential of component i in the standard state of component i, a_i is the activity of component i. The equilibrium condition 7 can then be written as:

$$\kappa\mu_K^0 + \alpha\mu_A^0 + n\mu_{H_2O}^0 - \mu_{K_\kappa A_\alpha nH_2O(s)} = -RT\ln(K_{K_\kappa A_\alpha nH_2O}) \tag{9}$$

where,

$$K_{K_k A_\alpha nH_2O} = a_K^\kappa a_A^\alpha a_{H_2O}^n \tag{10}$$

is the solubility product of the salt. The numerical value of the solubility product can be calculated by Equation 9. The composition of the liquid phase can be calculated by Equation 10. An m salt saturation point has to fulfill the condition 10 for all m salts:

$$K_k = \prod_i a_i^{\nu_{k,i}}, \quad k = 1,\ldots,m \tag{11}$$

while for all other salts potentially formed by the system,

$$K_k > \prod_i a_i^{\nu_{k,i}}, \quad k > m \tag{12}$$

In Equation 11 and 12, $\nu_{k,i}$ is the stoichiometric coefficient of component i in salt k. Equation 11 is solved by a full Newton-Raphson method using analytical composition derivatives of the activity coefficients. The m iteration variables are the amounts of each of the m salts in solution. The calculation of the points in quaternary solubility diagrams starts with the points where three solid phases are in equilibrium with a liquid phase. If the solubility products for all other salts are greater than the activity products of the salts, the solution represents a point where three solid phases are in equilibrium with a liquid phase. After that two salt lines are found. When the ends of a two salts line have been found, the line is approximated by a straight line providing start guess. After all points and lines in the diagram have been calculated then calculating the amount of water necessary to satisfy all solubility products begins. More information is provided by Thomsen [18]. Extended UNIQUAC model has produced good results for ionic system K^+, Na^+, Cl^-, NO_3^- in water. Comparison of extended UNIQUAC results with experimental data can be found in literature [18, 19].

4. Results and Discussion

4.1. Calculation of material balance

The problem that is solved in this paper can be defined as: A mixture of fixed composition is available (feed consists of KCl, $NaNO_3$ and water). Determine the streams flow rate that yields the desired product KNO_3 and by-product NaCl. In this problem two crystallizers as well as recycle of mother liquor is required. It is necessary to calculate ionic composition and water to total ions ratio at three points in the phase diagram, i.e. points K, L and M, before material balance. At point L, NaCl and at point M, KNO_3 crystallizes. Temperature of solutions L and M are 100 and 20°, respectively. The composition of solutions K, L and M are calculated by extended UNIQUAC model and are reported in Table 5. In other words, data reported in Table 5 are coordinates of points K, L and M in Janecke projection. Table 6 shows mole fraction of Na^+, K^+, Cl^-, NO_3^- and H_2O in points K, L and M calculated by data of Table 5. For example x_{Na^+} is calculated by:

$$x_{Na^+} = \frac{n_{Na^+}}{n_{Na^+} + n_{K^+} + n_{Cl^-} + n_{NO_3^-} + n_{H_2O}} \tag{13}$$

The process described in phase diagram is shown in Figure 3. The solutions K, L and M in Figure 2 corresponds to streams 2, 4 and 9 in Figure 3 (streams are shown in squares). In the first crystallizer, NaCl forms after adjusting amount of water by removing it as vapor at 100°. KNO_3 crystallizes in the second crystallizer at 20°. Water is added to feed of second crystallizer to adjust it to amount of necessary for crystallization of KNO_3. The method of depicting amount of water above Janecke projection and obtaining amount of water required for adding to feed of KNO_3 crystallizer is described in Mullin [9].

Simple design of crystallization processes can be achieved by trial and error. Therefore, a procedure for design of the process was developed. When the amount of desired product is chosen and temperature of crystallization of KNO_3 and NaCl is fixed, the solubility diagram shows the boundaries of operating region.

As depicted in Figure 3, NaCl is product of first crystallizer. It means that the amount of ions K^+ and NO_3^- that enters and exits from the crystallizer remains constant. Product of second crystallizer is KNO_3 and flow rate of ions Na^+ and Cl^- in the feed and effluent streams of this crystallizer does not change. Therefore, with regard to Figure 3 we can write mole balance for K^+, Na^+ and water in NaCl crystallizer as:

$$x_{K^+,2}F_2 = x_{K^+,3}F_3 \tag{14}$$

$$x_{Na^+,2}F_2 = x_{Na^+,3}F_3 + F_{NaCl} \tag{15}$$

$$x_{H_2O,2}F_2 = x_{H_2O,3}F_3 + F_4 \tag{16}$$

Streams 2 and 4 in Figure 3 are mixtures of ions K^+, Na^+, Cl^-, NO_3^- in water and F_2 and F_3 are total molar flow rate of ions and water. Reporting composition of F_2 and F_3 in terms of three salts is described in Mullin [9]. F_4 is molar flow rate of water evaporated in NaCl crystallizer.

F_{NaCl} is molar flow rate of produced crystals of NaCl which is known. $x_{K^+,2}$, $x_{Na^+,2}$ and $x_{H_2O,2}$ are mole fraction

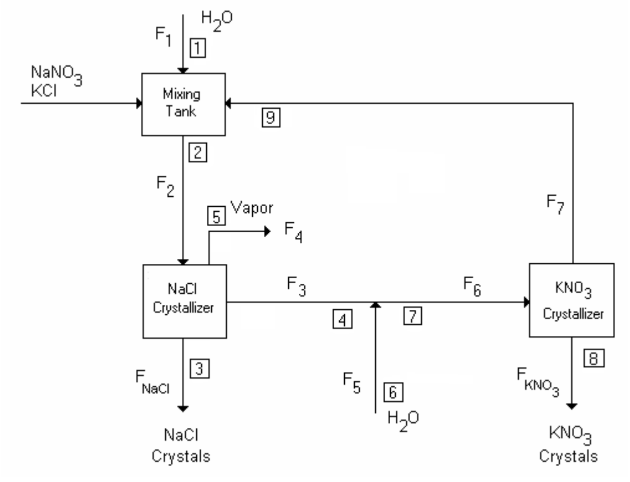

Figure 3: KNO_3 process labeled with total flow rate of streams. The numbers in squares are stream numbers

Table 7: Total ionic flow rate (sum of flow rates of ions and water) of streams shown in Figure 3

Stream	F_1	F_2	F_3	F_4	F_5	F_6	F_7
Kmol/h	45.0224	319.2782	209.4758	85.0224	40	249.4758	224.6958

of K^+, Na^+ and water in F_2 (solution K). $x_{K^+,3}$, $x_{Na^+,3}$ and $x_{H_2O,3}$ are mole fraction of K^+, Na^+ and water in F_3. Composition of streams F_2 (solution K), F_3 (solution L) and F_7 (solution M) are reported in Table 6.

The procedure established for calculation of mole balance is:

1. Guess the total molar flow rate of crystallizer feed (F_2).
2. Calculate F_3 by Equation 14.
3. Calculate F_{NaCl} by Equation 15.
4. Compare F_{NaCl} with known amount of it. If agreement does not exist, guess a new value for F_2 and repeat the calculations.
5. Calculate F_4 by Equation 16.

Similar calculations can be performed for second crystallizer knowing the value of produced KNO_3, F_{KNO_3}. Mole balance of Na^+, K^+ and water in second crystallizer are:

$$x_{Na^+,6}F_6 = x_{Na^+,7}F_7 \tag{17}$$

$$x_{K^+,6}F_6 = x_{K^+,7}F_7 + F_{KNO_3} \tag{18}$$

$$x_{H_2O,6}F_6 = x_{H_2O,7}F_7 \tag{19}$$

$x_{K^+,6}$, $x_{Na^+,6}$ and $x_{H_2O,6}$ are mole fraction of K^+, Na^+ and water in F_6. F_6 has been determined by adding F_5 to F_3. Therefore, F_7 can be calculated by Equation 17.

Table 8: Flow rate of ions and water in streams shown in Figure 3

Stream	1	2	3	4	5	6	7	8	9
F_{H_2O} (kmol/h)	45.02	212.55	-	127.53	85.02	40	167.53	-	167.53
F_{K^+} (kmol/h)	-	23.49	-	23.49	-	-	23.49	12.39	11.10
F_{Na^+} (kmol/h)	-	29.87	12.39	17.48	-	-	17.48	-	17.48
F_{Cl^-} (kmol/h)	-	29.87	12.39	17.48	-	-	17.48	-	17.48
$F_{NO_3^-}$ (kmol/h)	-	23.49	-	23.49	-	-	23.49	12.39	11.10

Table 9: Flow rate of salts and water in streams shown in Figure 3 calculated by data in Table 8

Stream	1	2	3	4	5	6	7	8	9
F_{H_2O} (kmol/h)	45.02	212.56	-	127.53	85.02	40	167.53	-	167.53
F_{KCl} (kmol/h)	-	23.49	-	17.48	-	-	17.48	-	11.1
F_{NaNO_3} (kmol/h)	-	23.49	-	17.48	-	-	17.48	-	11.1
F_{NaCl} (kmol/h)	-	6.39	12.39	-	-	-	-	-	6.39
F_{KNO_3} (kmol/h)	-	-	-	6.01	-	-	6.01	12.39	-

Amount of water added to mixing tank (F_1) can be achieved by water mole balance in mixing tank knowing F_2 and F_7:

$$F_1 + x_{H_2O,7}F_7 = x_{H_2O,2}F_2 \tag{20}$$

The results of handy material balance for production of 12.39 kmol/h KNO_3 are reported in Tab. 7 and 8. Referring to the stoichiometry of reaction, production of 12.39 kmol/h KNO_3 requires 12.39 kmol/h KCl and $NaNO_3$. The results reported in Table 8 are based on ionic flow rate of solutions. In the other words, the results are flow rate of ions and water in solutions that are calculated by Equations 14-20. These data can be transformed to flow rates of salts as shown in Table 9.

5. Conclusion

For design of KNO_3 production process it is necessary to determine material balance. Thermodynamics of electrolyte mixtures is needed to establish equilibrium composition of process streams. Extended UNIQUAC model was used to calculate phase diagram of process containing K^+, Na^+, Cl^-, NO_3^- ions in water at different temperatures. Hence, composition of streams in process was calculated. Based on ion conservation in crystallizers, a simple and handy method was presented to calculate flow rate of all salts and water.

Nomenclature

α	number of anions in salt
κ	number of cations in salt
μ_i	chemical potential of component i (J mol^{-1})
μ_i^0	chemical potential of component *i* at standard state (J mol^{-1})
$\nu_{k,i}$	stoichiometric coefficient of component *i* in salt *k*
a_i	activity of component *i*
F_i	total molar flow rate of ions and water in stream *i* (kmol h^{-1})
G^E	excess Gibbs free energy (J mol^{-1})
G^E_{LR}	long-range contribution of excess Gibbs free energy (J mol^{-1})
G^E_{SR}	short-range contribution of excess Gibbs free energy (J mol^{-1})
K	solubility product
n	number of water molecules in salt
n_i	number of moles of component *i*
q_i	surface area parameter of component *i* in extended UNIQUAC
R	gas constant (J $mol^{-1}K^{-1}$)

r_i	volume parameter of component i in extended UNIQUAC
T	Temperature (K)
u_{kl}	UNIQUAC interaction parameter (K)
x_i	mole fraction of component i
$x_{i,j}$	mole fraction of component i in stream j

References

[1] Ng KM, *Systematic separation of a multicomponent mixture of solids based on selective crystallization and dissolution*, Separations Technology, 1991. **1**(2):pp. 108 – 120. doi:10.1016/0956-9618(91)80006-L

[2] Cisternas LA and Rudd DF, *Process designs for fractional crystallization from solution*, Industrial & Engineering Chemistry Research, 1993. **32**(9):pp. 1993–2005. doi:10.1021/ie00021a022

[3] Dey SR and Ng KM, *Fractional crystallization: Design alternatives and tradeoffs*, AIChE Journal, 1995. **41**(11):pp. 2427–2438. doi:10.1002/aic.690411109

[4] Berry DA and Ng KM, *Separation of quaternary conjugate salt systems by fractional crystallization*, AIChE Journal, 1996. **42**(8):pp. 2162–2174. doi:10.1002/aic.690420808

[5] Cisternas LA and Swaney RE, *Separation System Synthesis for Fractional Crystallization from Solution Using a Network Flow Model*, Industrial & Engineering Chemistry Research, 1998. **37**(7):pp. 2761–2769. doi:10.1021/ie970335y

[6] Cisternas LA, *Optimal design of crystallization-based separation schemes*, AIChE Journal, 1999. **45**(7):pp. 1477–1487. doi:10.1002/aic.690450711

[7] Cisternas LA, Guerrero CP and Swaney RE, *Separation system synthesis of fractional crystallization processes with heat integration*, Computers & Chemical Engineering, 2001. **25**(4-6):pp. 595 – 602. doi:10.1016/S0098-1354(01)00639-1

[8] Purdon F and Slater V, *Aqueous solution and the phase diagram*, E. Arnold & Co., London, 1946

[9] Mullin JW, *Crystallization*, Butterworth-Heinemann, Oxford, 4th edition, 2001

[10] Fitch B, *How to Design Fractional Crystallization Processes*, Industrial & Engineering Chemistry, 1970. **62**(12):pp. 6–33. doi:10.1021/ie50732a004

[11] Cesar MAB and Ng KM, *Improving Product Recovery in Fractional Crystallization Processes: Retrofit of an Adipic Acid Plant*, Industrial & Engineering Chemistry Research, 1999. **38**(3):pp. 823–832. doi:10.1021/ie9803671

[12] Thomsen K, Rasmussen P and Gani R, *Simulation and optimization of fractional crystallization processes*, Chemical Engineering Science, 1998. **53**(8):pp. 1551 – 1564. doi:10.1016/S0009-2509(97)00447-8

[13] Cisternas LA, Torres MA, Godoy MJ and Swaney RE, *Design of separation schemes for fractional crystallization of metathetical salts*, AIChE Journal, 2003. **49**(7):pp. 1731–1742. doi:10.1002/aic.690490712

[14] Cisternas L, Cueto J and Swaney R, *Flowsheet synthesis of fractional crystallization processes with cake washing*, Computers & Chemical Engineering, 2004. **28**(5):pp. 613 – 623, eSCAPE 13. doi:10.1016/j.compchemeng.2004.02.006

[15] Thomsen K, Rasmussen P and Gani R, *Correlation and prediction of thermal properties and phase behaviour for a class of aqueous electrolyte systems*, Chemical Engineering Science, 1996. **51**(14):pp. 3675 – 3683. doi:10.1016/0009-2509(95)00418-1

[16] Thomsen K and Rasmussen P, *Modeling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems*, Chemical Engineering Science, 1999. **54**(12):pp. 1787 – 1802. doi:10.1016/S0009-2509(99)00019-6

[17] Iliuta MC, Thomsen K and Rasmussen P, *Extended UNIQUAC model for correlation and prediction of vapour-liquid-solid equilibria in aqueous salt systems containing non-electrolytes. Part A. Methanol-water-salt systems*, Chemical Engineering Science, 2000. **55**(14):pp. 2673 – 2686. doi:10.1016/S0009-2509(99)00534-5

[18] Thomsen K, *Aqueous Electrolytes: Model Parameters and Process Simulation*, Ph.D. thesis, Technical University of Denmark, 1997

[19] Thomsen K, *Simulation and Design of Processes with Electrolyte Mixtures*, Master's thesis, Technical University of Denmark, 1994