Synthesis of Crystallization-Based Separation Systems

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Outline

- Crystallization design problem overview
- Fractional Crystallization
- Fractional Crystallization with Heat Integration & Cake Washing
- Final Remark

Crystallization design problem overview

- **Crystallization is extensively used in different industrial applications, including the production of a wide range of materials such as fertilizers, detergents, foods, and pharmaceutical products, as well as in the treatment of waste effluents**

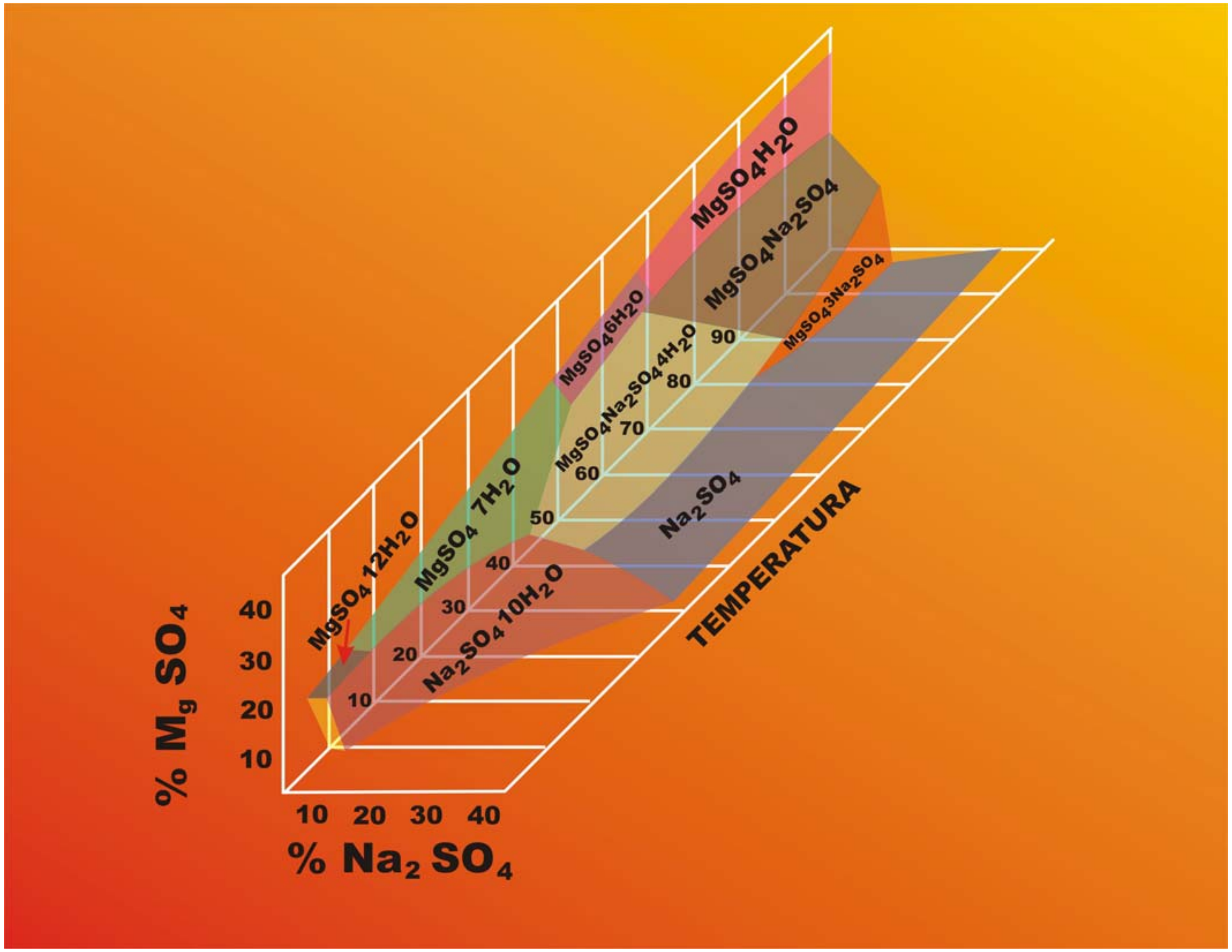
Problems

- The crystallization stages are usually accompanied by other separation techniques. Leaching.
- Various types of crystallization exist: cooling, evaporation, reactions, and drowning-out
- The characteristics of the product affects a series of other associated operations. filtration & washing.
- The separation is limited by multiple saturation points. Temperature changes & external chemical agents.
- Kinetic factors and metastability may affect the design.

Phase Diagram

- The greatest advantages obtained in the use of the phase diagram are the possibilities for the visualization of the behavior of phase equilibria, describing the processes, and obtaining mass balances with the help of the lever arms rule.
- The phase diagrams, however, also have a series of limitations as a design tool

Phase Diagram



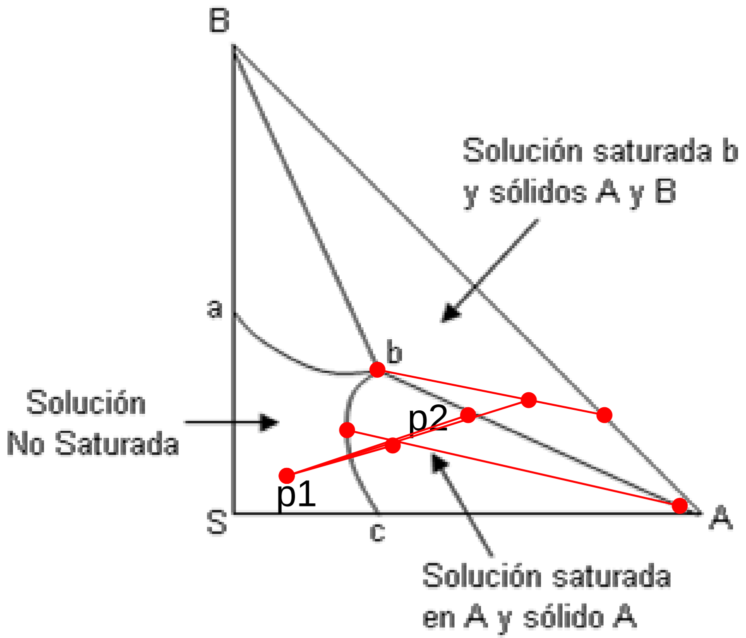
Goals

- Determine optimal stream configuration.
- Determine operational conditions & flowrates.
- Selection of equipment type.
- Determine solid-liquid separation. Washing & Filtration.
- Determine heat integration.

Fractional Crystallization

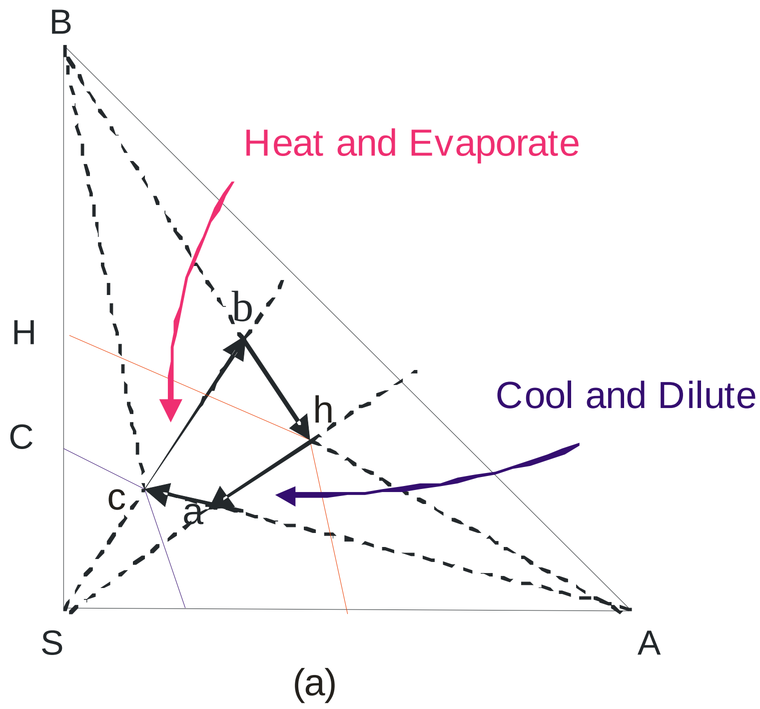
- Basic Crystallization Separation
- Relative Composition Diagram
- Feasible Pathway Diagram
- State Superstructure
- Connectivity Matrix
- Mathematical model
- Examples

Basic Crystallization Separation



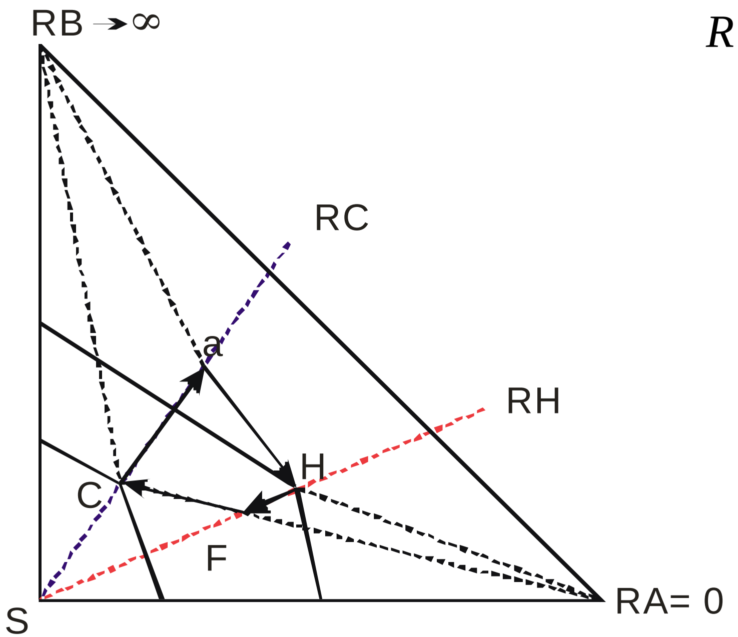
Isothermal Cut
KCl+NaCl+H2O
KNO3+NaNO3+H2O
L serine acid + L aspartic acid + water

Basic Crystallization Separation



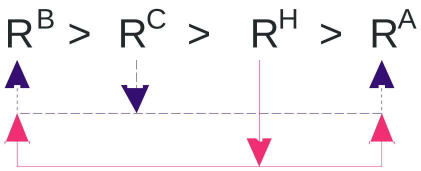
Basic Cycle

Relative Composition Diagram

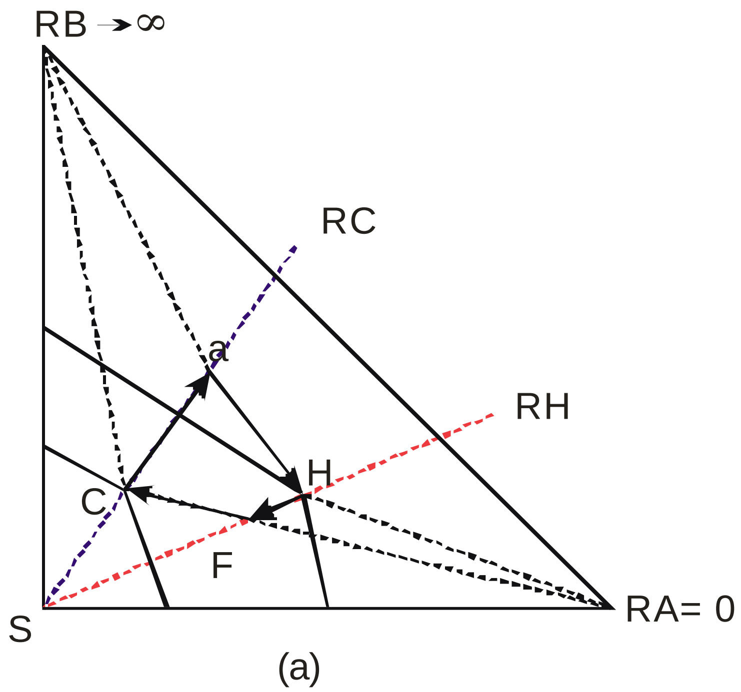


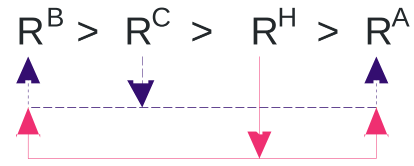
(a)

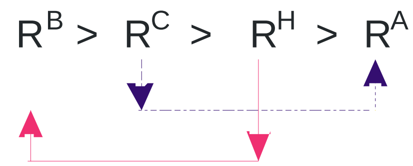
$$R = \frac{\text{Weight Composition of B}}{\text{Weight Composition of A}}$$



Feasible Pathway Diagram

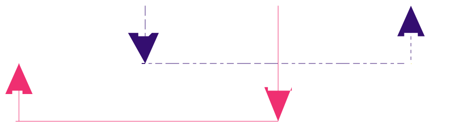


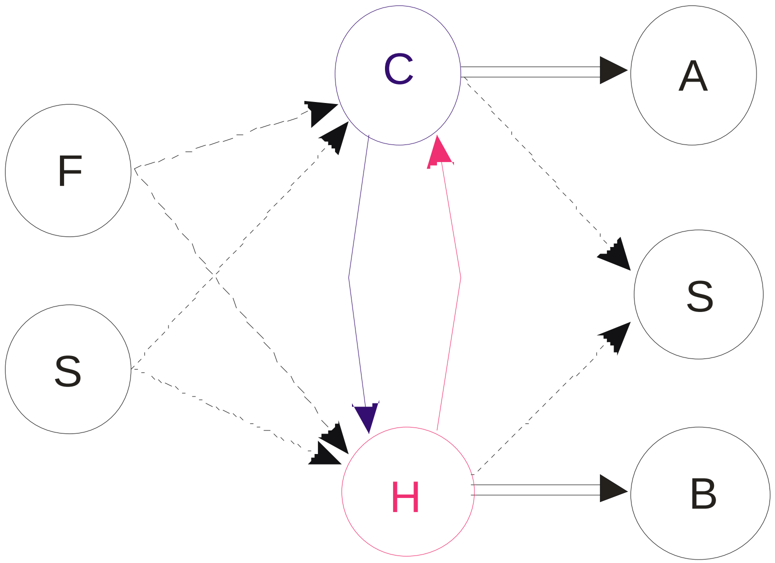




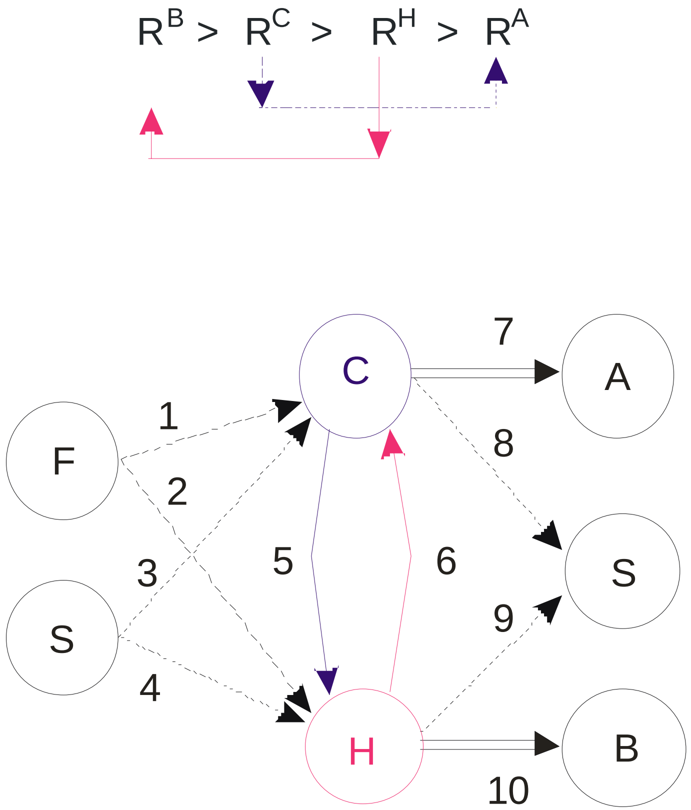
State Superstructure

$R^B > R^C > R^H > R^A$



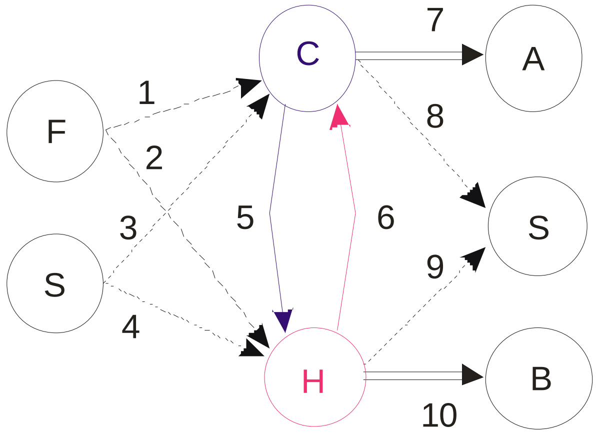


Connectivity Matrix



	C	H	S_2	A	B
F	1	2			
S_1	3	4			
C		5	8	7	
H	6		9		10

Mathematical model



General model
Cisternas, L.A. (1999), Optimal design of crystallization-based separation schemes, *AIChE J.*, 45, 1477-1487.

$$\underset{w}{Min} \sum_{l} w_l$$

$$w_1 \ x_{1,i} + w_3 \ x_{3,i} + w_6 \ x_{6,i} = w_5 \ x_{5,i} + w_7 \ x_{7,i} + w_8 \ x_{8,i}$$

$$w_2 \ x_{2,i} + w_4 \ x_{4,i} + w_5 \ x_{5,i} = w_6 \ x_{6,i} + w_9 \ x_{9,i} + w_{10} \ x_{10,i}$$

$$w_1 \ x_{1,i} + w_2 \ x_{2,i} = C_{1,i}^F$$

$$w_l \geq 0; \quad i = A, B, S$$

Examples-Sylvinite

Production of potassium chloride from 100,000 ton/year of sylvinite (47.7% KCl, 52.3% NaCl).

Equilibrium Data

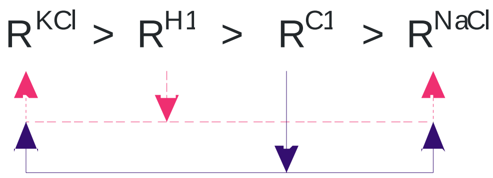
key	Temperature [°C]	Weight Composition		Solid Phase
		KCl	NaCl	
C1	30	11.7	20.25	KCl+NaCl
H1	100	22.2	15.9	KCl+NaCl

R_{KCl}	R_{H1}	R_{C1}	R_{NaCl}
∞	1.40	0.58	0.0

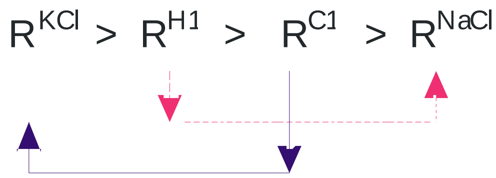
Fractional Crystallization

Examples-Sylvinite

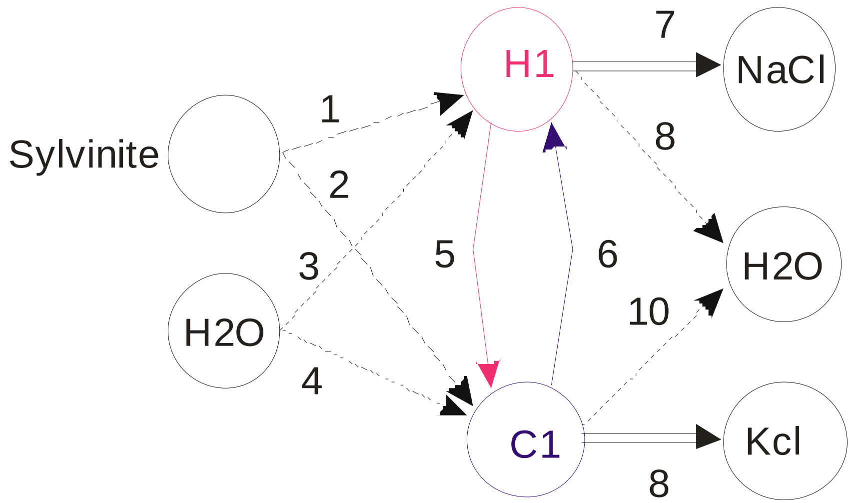
Relative Composition Diagram



Feasible Pathway Diagram

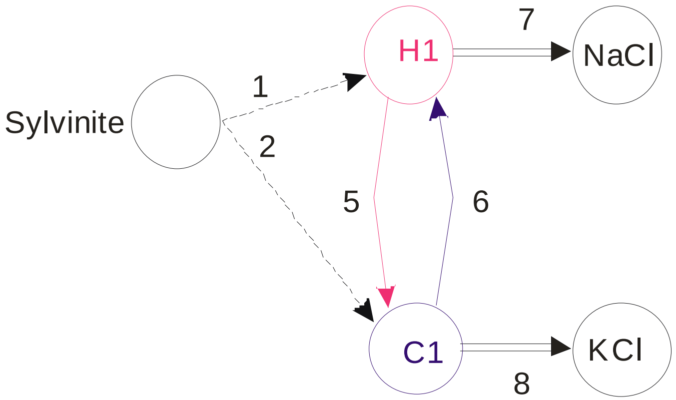


State Diagram

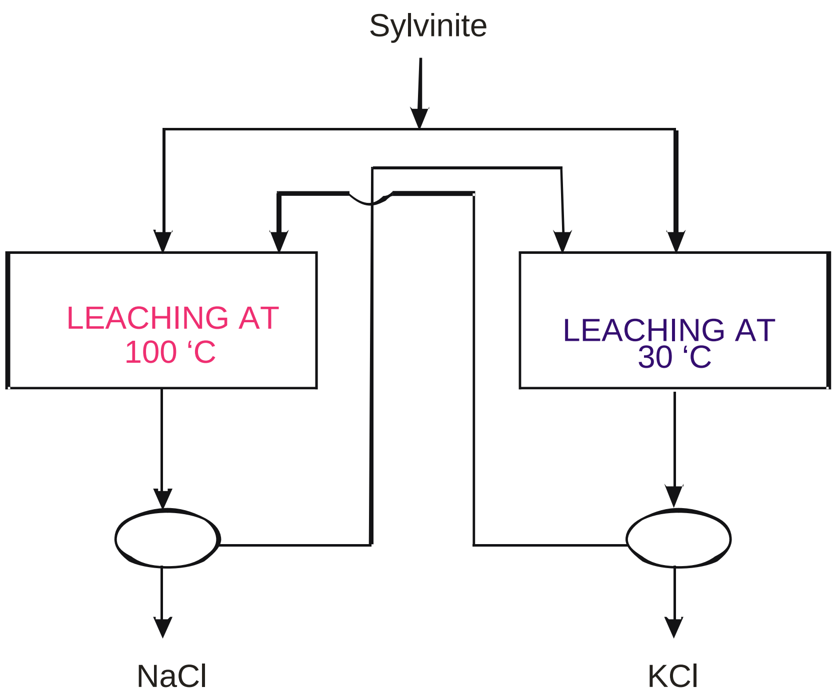


Examples-Sylvinite

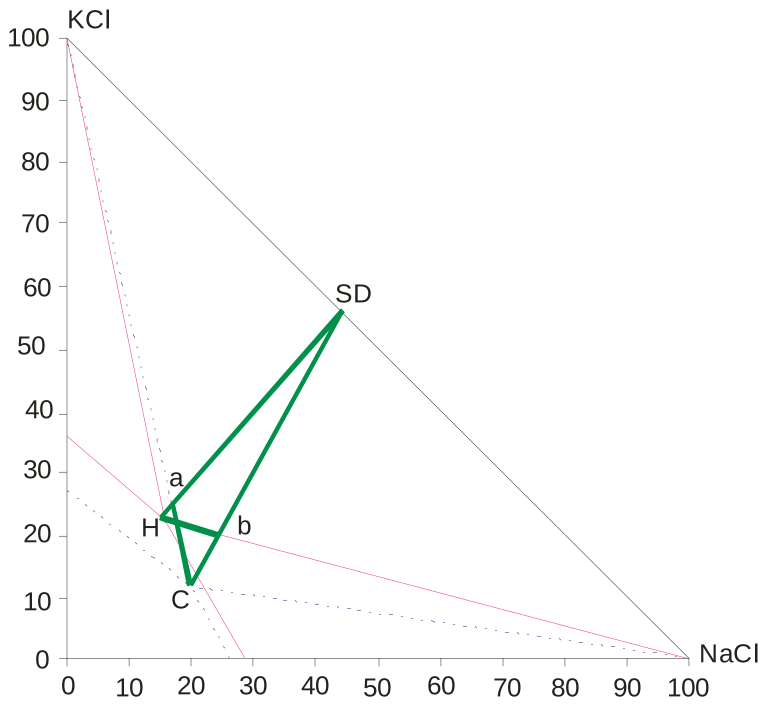
State Diagram



Flow Sheet



Examples-Sylvinite



Sylvinite.gms

Fractional Crystallization

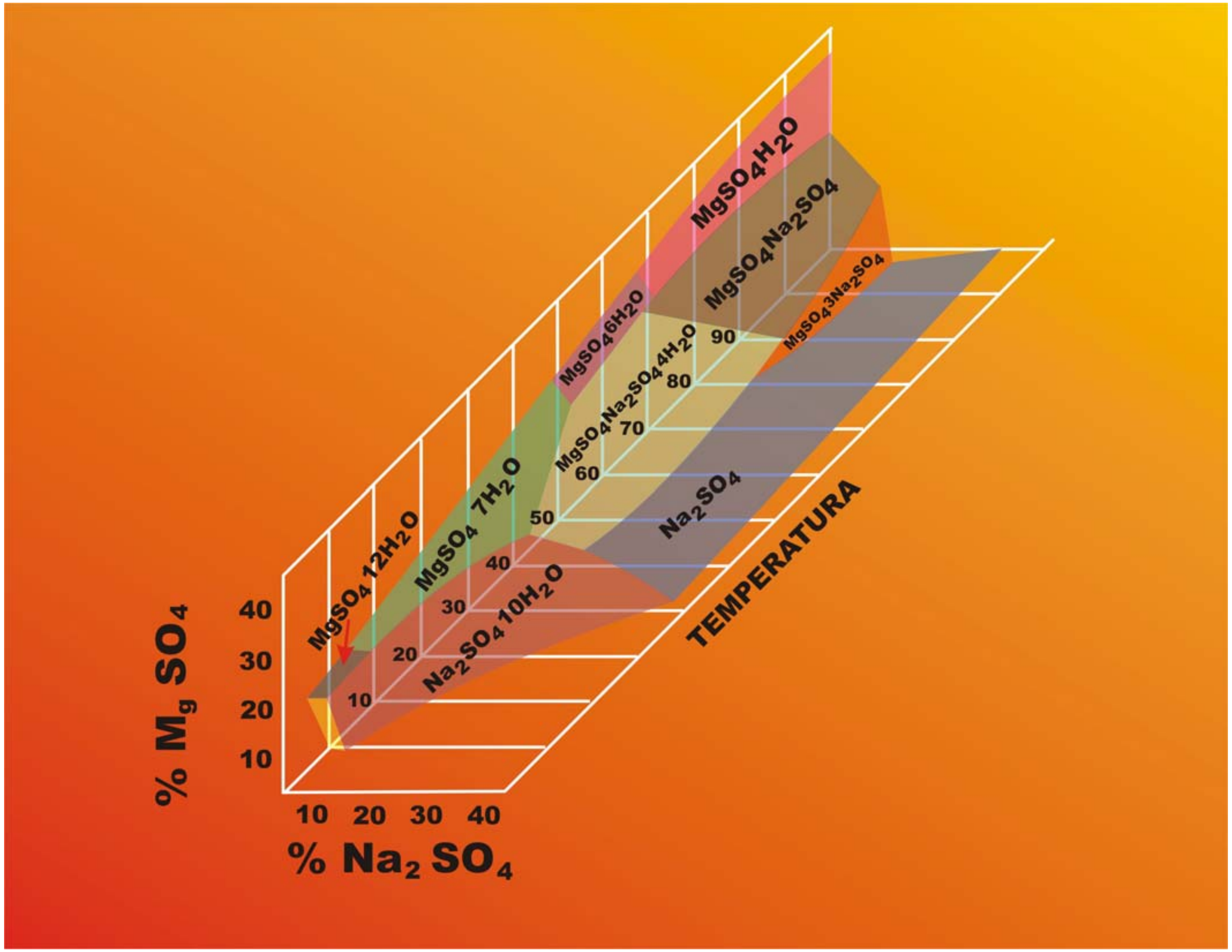
Examples-Astrakanite

Equilibrium data for $MgSO_4+Na_2SO_4+H_2O$ system.

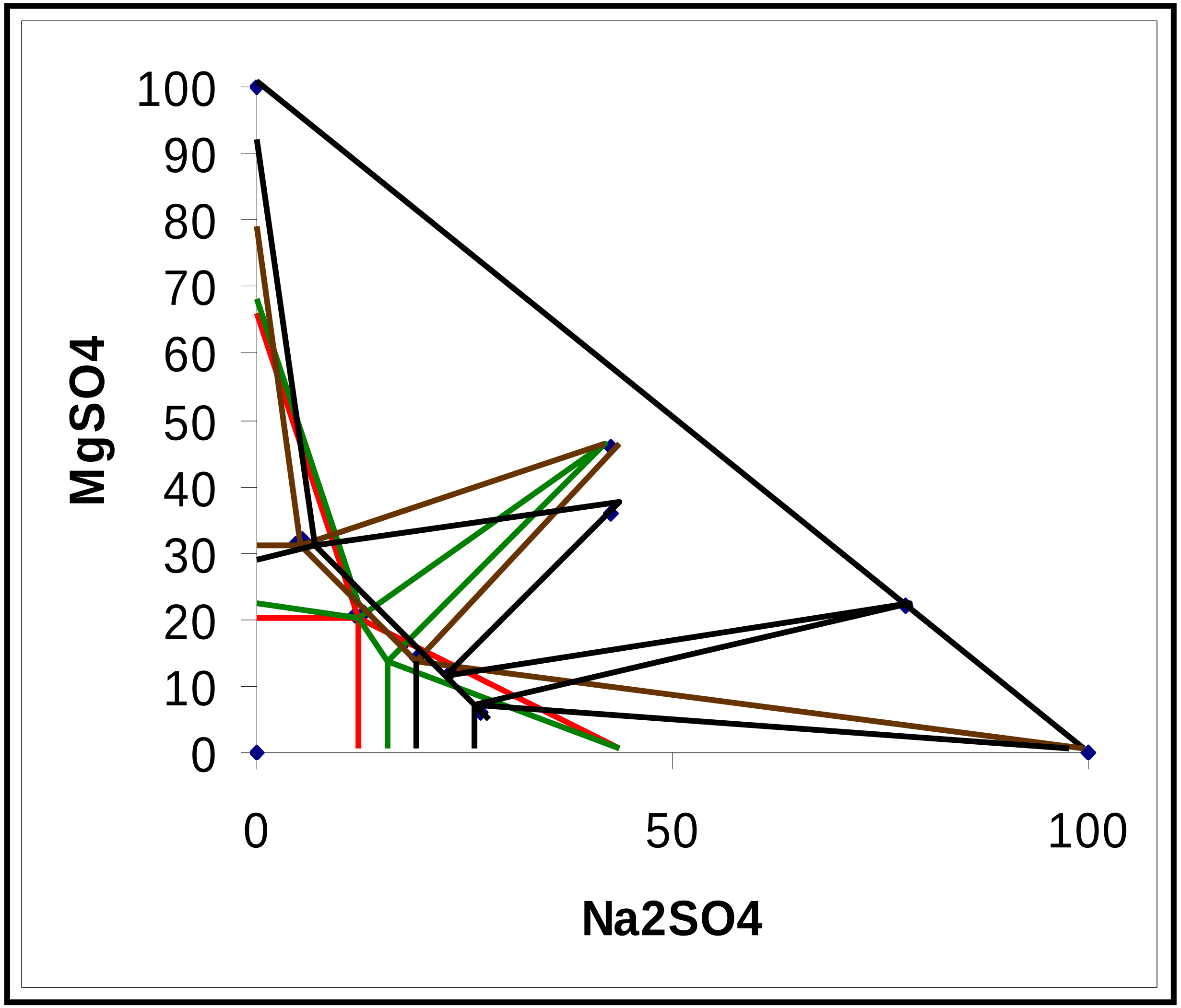
T ºC	keys	Saturated solution, % w		Solid phase	R
		$MgSO_4$	Na_2SO_4		
18.7	C	20.57	11.8	Mg_7 + Na_{10}	1.7
25	D1	21.15	13	Mg_7 + SD1	1.6
25	D2	16.6	17.8	SD1 + Na_{10}	0.9
50	E1	31.32	4.74	Mg_6 + SD1	6.6
50	E2	11.98	23.25	SD1 + Na	0.5
97	F1	32.2	5.55	Mg_1 + SD2	5.8
97	F2	14.4	19.15	SD2 + SD3	0.8
97	F3	5.88	26.9	SD3 + Na	0.2
	SD1	35.99	42.48		0.8
	SD2	45.86	54.14		0.8
	SD3	22.02	77.98		0.3

Mg7=MgSO4.7H2O; Mg1=MgSO4.1H2O; Mg6=MgSO4.6H2O; Na10=Na2SO4.10H2O; Na=Na2SO4; SD1= Na2SO4.MgSO4.4H2O; SD2= Na2SO4.MgSO4; SD3= MgSO4.3Na2SO4

Phase Diagram

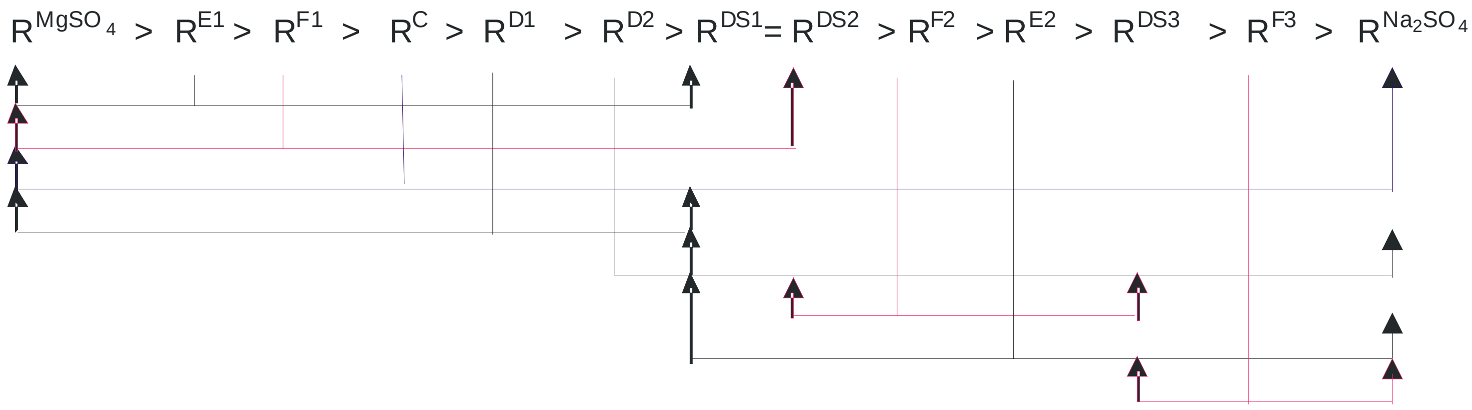


Isothermal Cuts

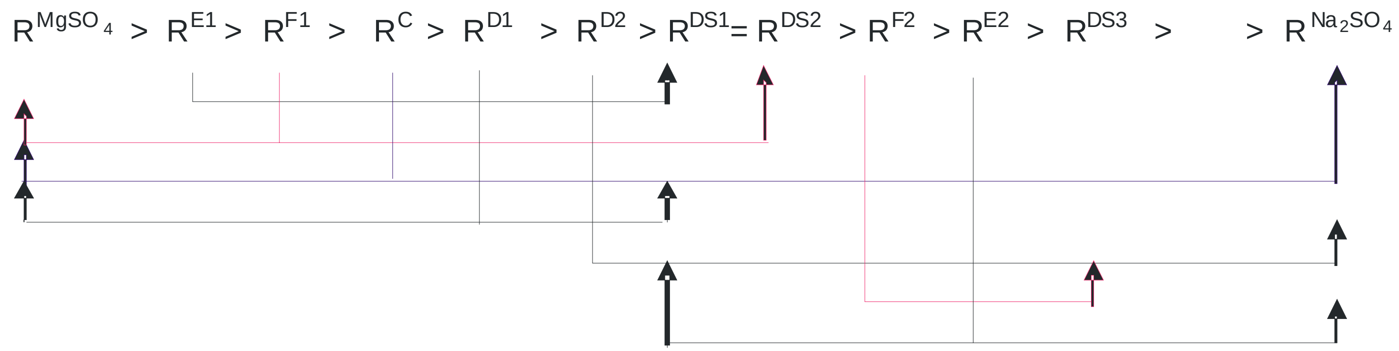


Examples-Astrakanite

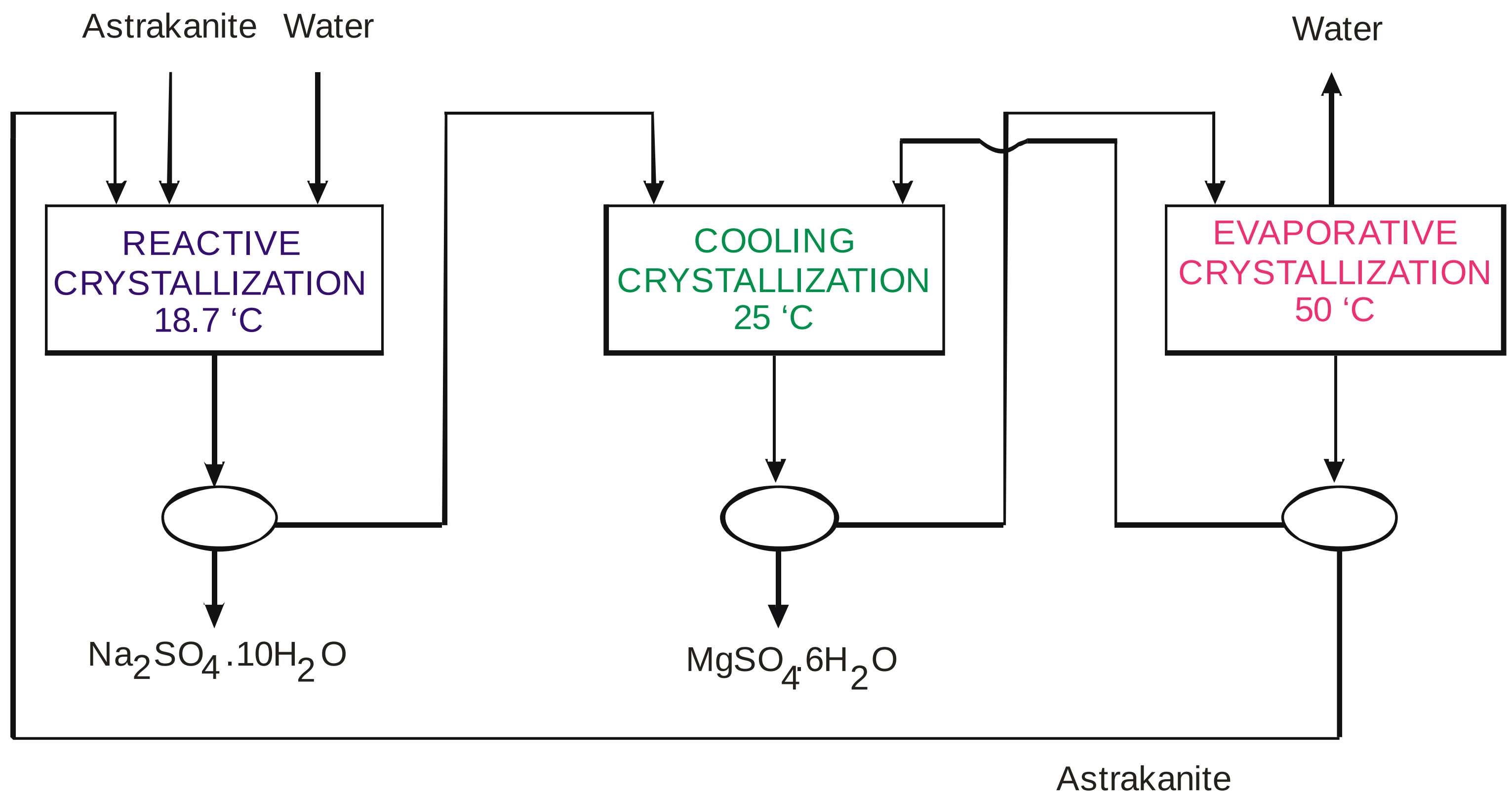
Relative Composition Diagram



Feasible Pathway Diagram



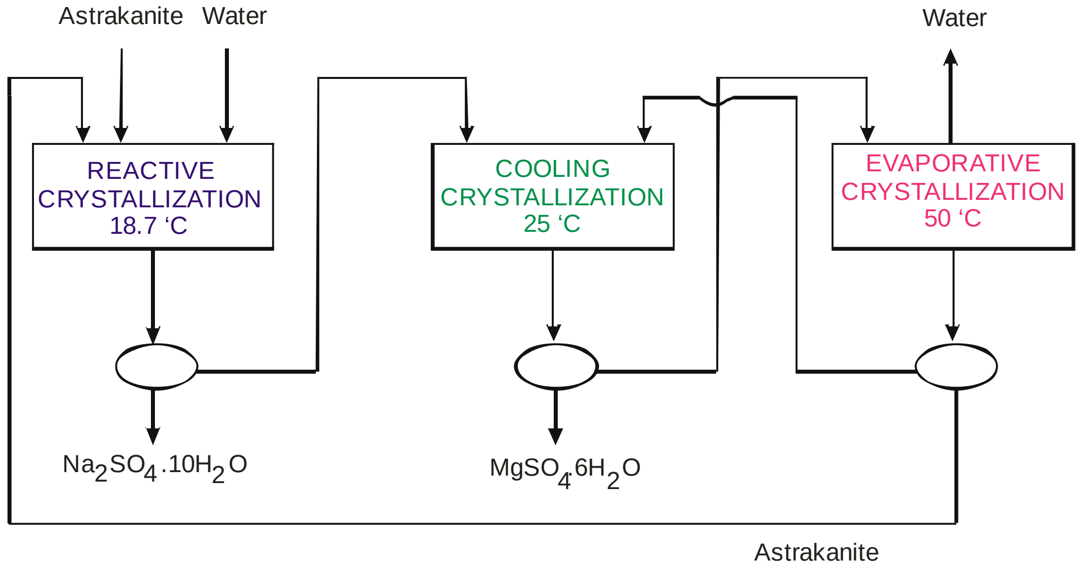
Examples-Astrakanite



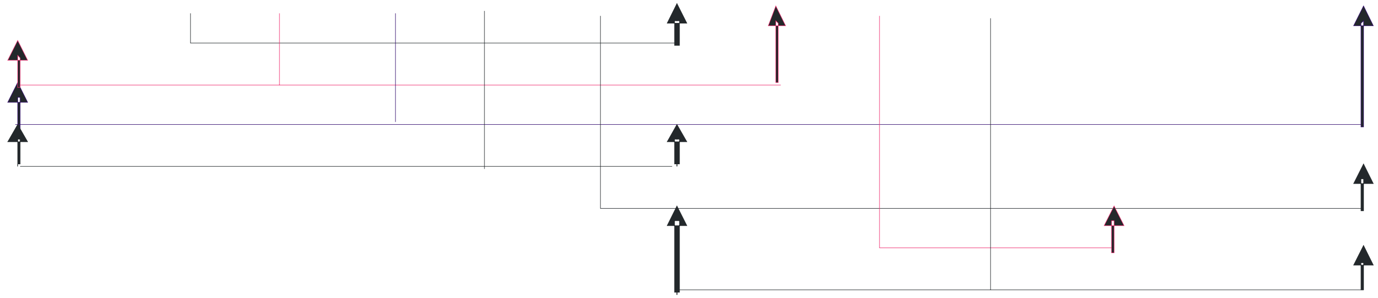
astrakanite.gms

Examples-Astrakanite

C 18.7 °C
D1 25 °C
E1 50 °C



$R^{MgSO_4} > R^{E1} > R^{F1} > R^{C} > R^{D1} > R^{D2} > R^{DS1} = R^{DS2} > R^{F2} > R^{E2} > R^{DS3} > \quad > R^{Na_2SO_4}$



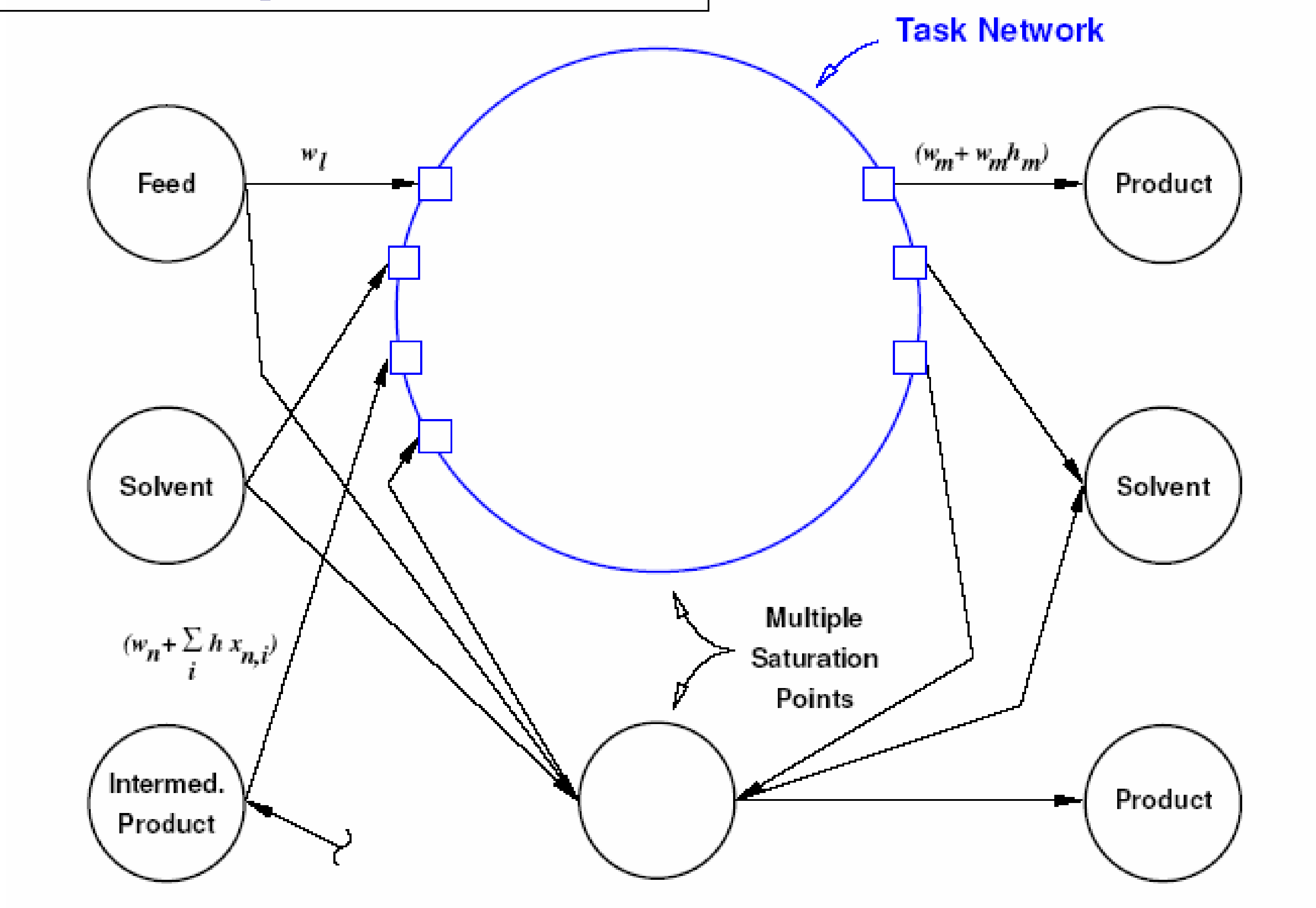
Fractional Crystallization with Heat Integration & Cake Washing

- State Superstructure
- Task superstructure.
- Heat integration.
- Cake Washing

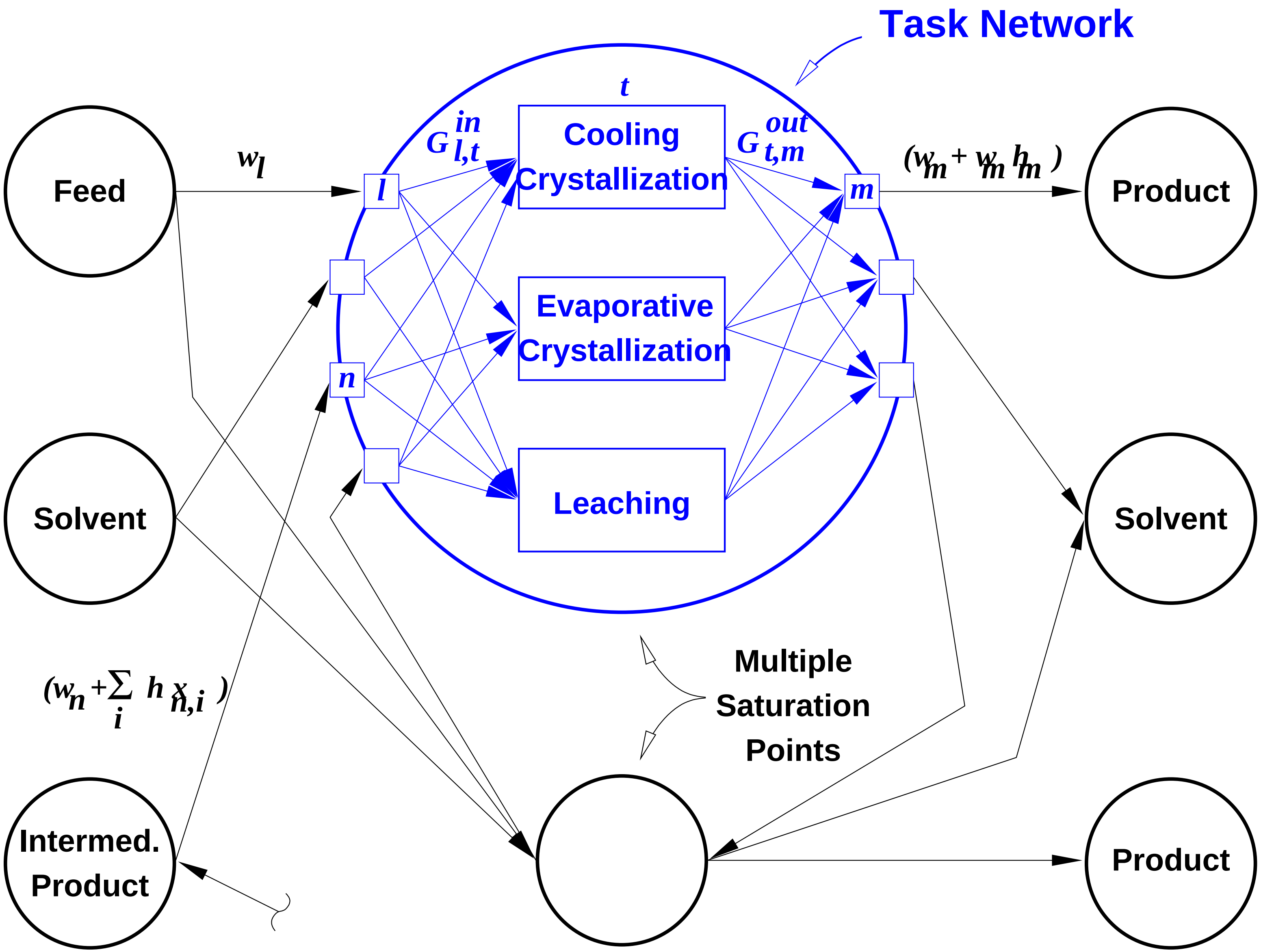
•Cisternas L.A., J.Y. Cueto and R.E. Swaney, "Flowsheet Synthesis of Fractional Crystallization Process with Cake Washing", *Computer and Chemical Engineering*, 28, 613-623 (2004)

• Cisternas L.A., C. Guerrero and R. Swaney,, "Separation System Synthesis of Fractional Crystallization Processes with Heat Integration", *Computer and Chemical Engineering*, 25, 595-602 2001

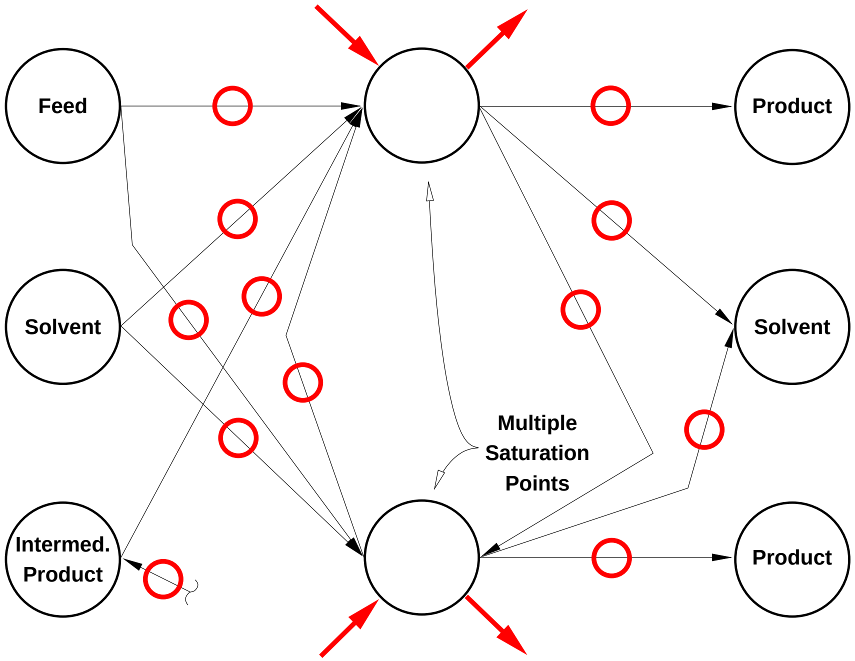
Task Superstructure

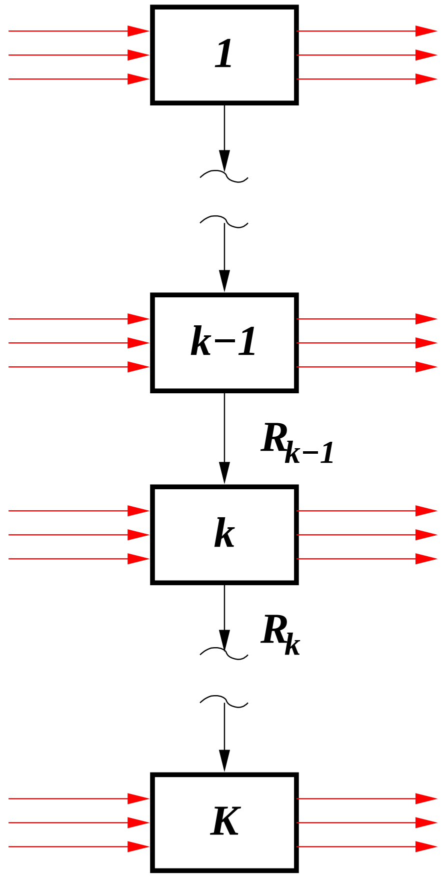


Fractional Crystallization with Heat Integration 6 Cake Washing



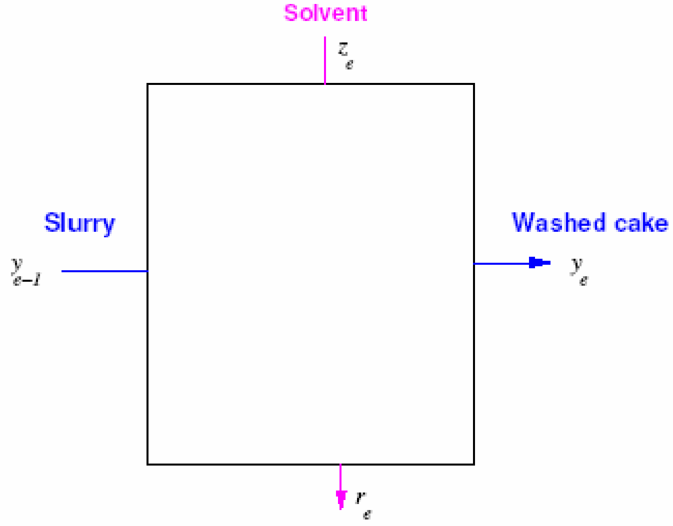
Heat Integration

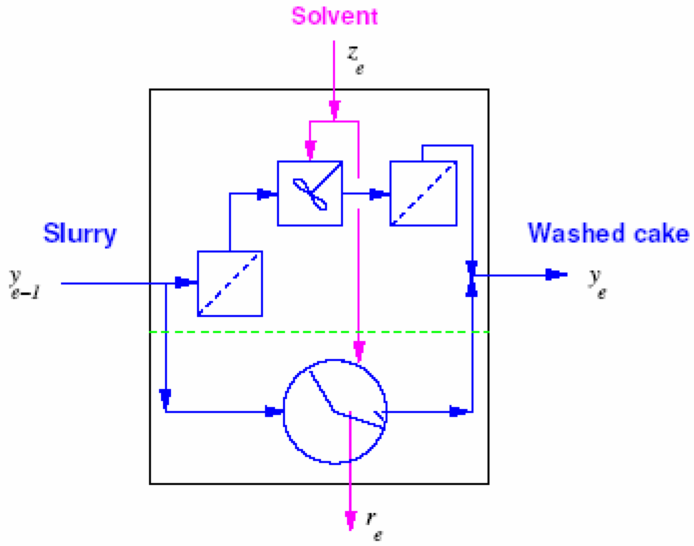




Papoulias S.A., & I.E. Grossmann (1983), A structural optimization approach to process synthesis-II. Heat recovery networks. Comp. and Chem. Engng., 7, 707

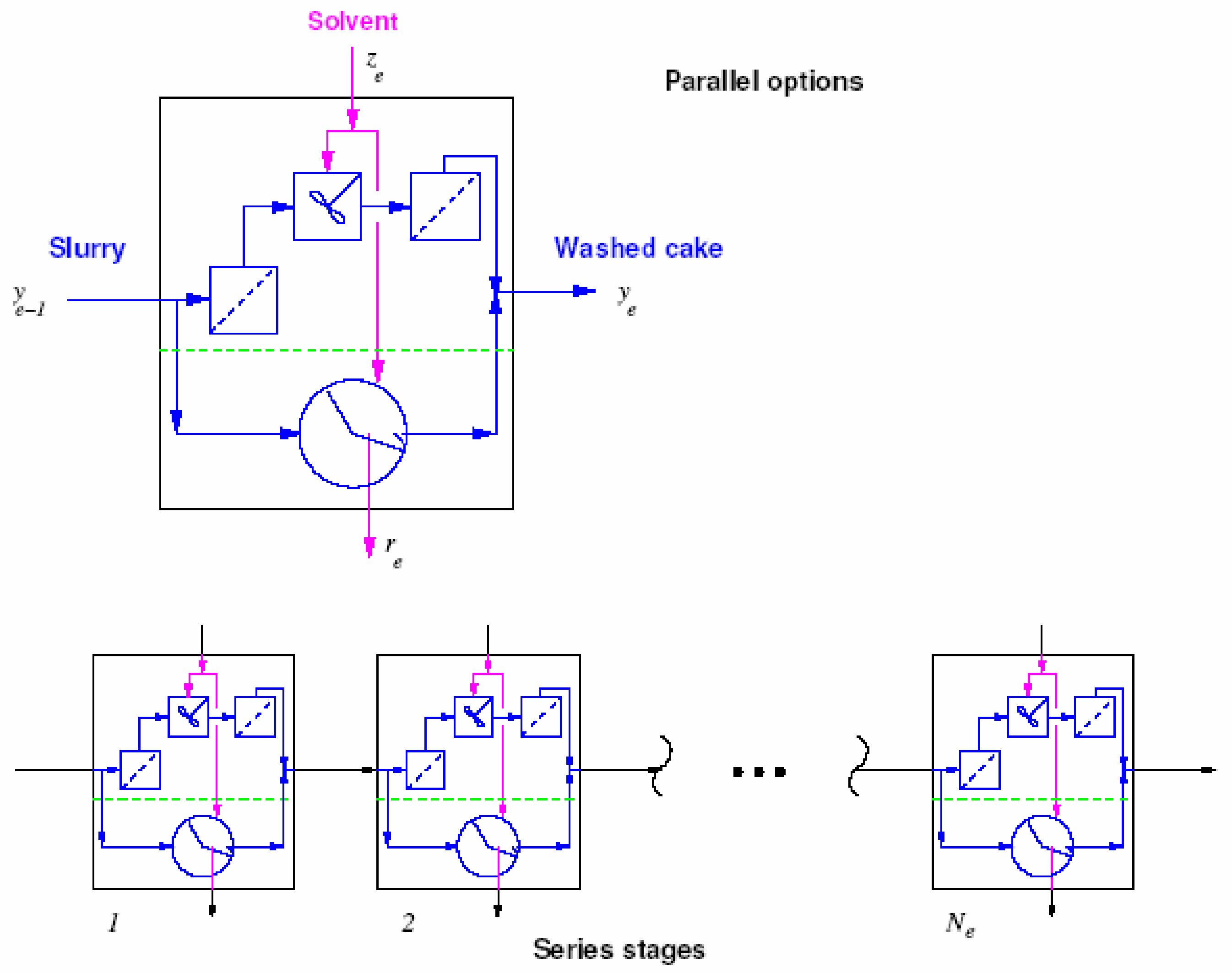
Cake Washing





Parallel Options

Fractional Crystallization with Heat Integration & Cake Washing



Mathematical Model

State Superstructure

Mass balance for each component in multiple saturation nodes (*SM*):

$$\sum_{l \in Lq \cap S^{in}(s)} hx_{l,i} + \sum_{l \in S^{in}(s)} w_l \cdot x_{l,i} - \sum_{l \in S^{out}(s)} w_l \cdot x_{l,i} - \sum_{l \in (Lw \cup Lq) \cap S^{out}(s)} w_l h_l x_{l',i} = 0 \qquad s \in S_M, i \in I$$

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

$$\sum_{l \in Lq \cap S^{in}(s)} w_l \cdot x_{l,i} - \sum_{l \in Lq \cap S^{out}(s)} w_l \cdot x_{l,i} = 0 \qquad s \in S_I, i \in I$$

$$\sum_{l \in Lq \cap S^{out}(s)} hx_{l,i} - \sum_{l \in Lq \cap S^{in}(s)} w_l \; h_l x_{l',i} = 0 \qquad s \in S_I, i \in I$$

$$\sum_{i \in I} (w_l \cdot x_{l,i} + hx_{l,i}) - U_l \; ym_l \leq 0 \qquad l \in Lq \cap S^{out}(s), s \in S_I$$

$$\sum_{l \in Lq \cap S^{out}(s)} ym_l - 1 = 0 \qquad s \in S_I$$

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

$$\sum_{l \in S^{out}(s)} w_l \cdot x_{l,i} = C^F_{s,i} \qquad s \in S_F, i \in I_F(s)$$

Task Superstructure

Mass balance between the thermodynamic state network and task network

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

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

Mass balance in the task network:

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

Task selection and energy balance:

$$\begin{bmatrix} y_{t,s} \\ FC_{t,s} = \alpha_{t,s} \\ VC_{t,s} = \beta_{t,s} \sum_{l \in S^{in}(s)} G_{l,t}^{in} \\ Q_{t,s}^{C} = HQ_{t,s}^{C} G_{t,l1}^{out} + HQ_{t,s}^{D} G_{l2,t}^{in}, l1 \in S_d^{out}(s), l2 \in S_d^{in}(s) \\ Q_{t,s}^{S} = HS_{t,s} G_{t,l}^{out}, l \in S_s^{out}(s) \end{bmatrix} \vee \begin{bmatrix} \neg y_{t,s} \\ FC_{t,s} = 0 \\ VC_{t,s} = 0 \\ Q_{t,s}^{C} = 0 \\ Q_{t,s}^{S} = 0 \end{bmatrix} \quad t \in T(s), s \in S_M(s)$$

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

Cake Washing

Mass balance for each component in wash/reslurry stage:

$$ypw_{l,e,i} + nw_{l,e}\ zw_{l,e,i} - ymw_{l,e,i} - rw_{l,e,i}\ nw_{l,e} = 0 \qquad l \in Lw,\ e \in E(Lw),\ i \in I$$

$$ypr_{l,e,i} + nr_{l,e}\ zr_{l,e,i} - ymr_{l,e,i} - rr_{l,e,i}\ nr_{l,e} = 0$$

Efficiency constraint for wash/reslurry stage:

$$Ew_{l,e,i}\ rw_{l,e,i} - Ew_{l,e,i}\ ypw_{l,e,i} - ymw_{l,e,i} + ypw_{l,e,i} = 0 \quad l \in Lw,\ e \in E(Lw),\ i \in I$$

$$Er_{l,e,i}\ rr_{l,e,i} - Er_{l,e,i}\ ypr_{l,e,i} - ymr_{l,e,i} + ypr_{l,e,i} = 0$$

Degree of impurity:

$$y_{l,\bar{E},i}\ h_l \le IL_{l,i} \qquad l \in Lw,\ i \in I$$

Wash or reslurry/filter selection:

$$
\begin{bmatrix}
yw_{l,e} \\
\neg yr_{l,e} \\
y_{l,e,i} = ymw_{l,e,i} \\
ypw_{l,e,i} = y_{l,e-1,i} \\
ymr_{l,e,i} = 0 \\
ypr_{l,e,i} = 0 \\
zw_{l,e,i} = z_{l,e,i} \\
zr_{l,e,i} = 0 \\
Qw_{l,e} = nw_{l,e} h_l \ w_l^0 \\
Qr_{l,e} = 0 \\
Cf_{l,e} = Cfw \\
Cv_{l,e} = Cvw\ Qw_{l,e} + \\
\quad Cs\ Qw_{l,e}
\end{bmatrix}
\vee
\begin{bmatrix}
\neg yw_{l,e} \\
yr_{l,e} \\
y_{l,e,i} = ymr_{l,e,i} \\
ypr_{l,e,i} = y_{l,e-1,i} \\
ymw_{l,e,i} = 0 \\
ypw_{l,e,i} = 0 \\
zw_{l,e,i} = 0 \\
zr_{l,e,i} = z_{l,e,i} \\
Qw_{l,e} = 0 \\
Qr_{l,e} = nr_{l,e} h_l \ w_l^0 \\
Cf_{l,e} = Cfr + Cff \\
Cv_{l,e} = Cvr\ (Qr_{l,e} + w_l^0) \\
\quad Cvf\ \ Qr_{l,e} + Cs\ Qr_{l,e}
\end{bmatrix}
\vee
\begin{bmatrix}
\neg yw_{l,e} \\
\neg yr_{l,e} \\
y_{l,e,i} = y_{l,e,i} \\
ymr_{l,e,i} = 0 \\
ypr_{l,e,i} = 0 \\
ymw_{l,e,i} = 0 \\
ypw_{l,e,i} = 0 \\
zw_{l,e,i} = 0 \\
zr_{l,e,i} = z_{l,e,i} \\
Qw_{l,e} = 0 \\
Qr_{l,e} = 0 \\
Cf_{l,e} = 0 \\
Cv_{l,e} = 0
\end{bmatrix}
\quad
\begin{matrix} e \in E(Lw), \\ l \in Lw, i \in I \end{matrix}
$$

Heat Integration

Heat balance around each temperature interval k:

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

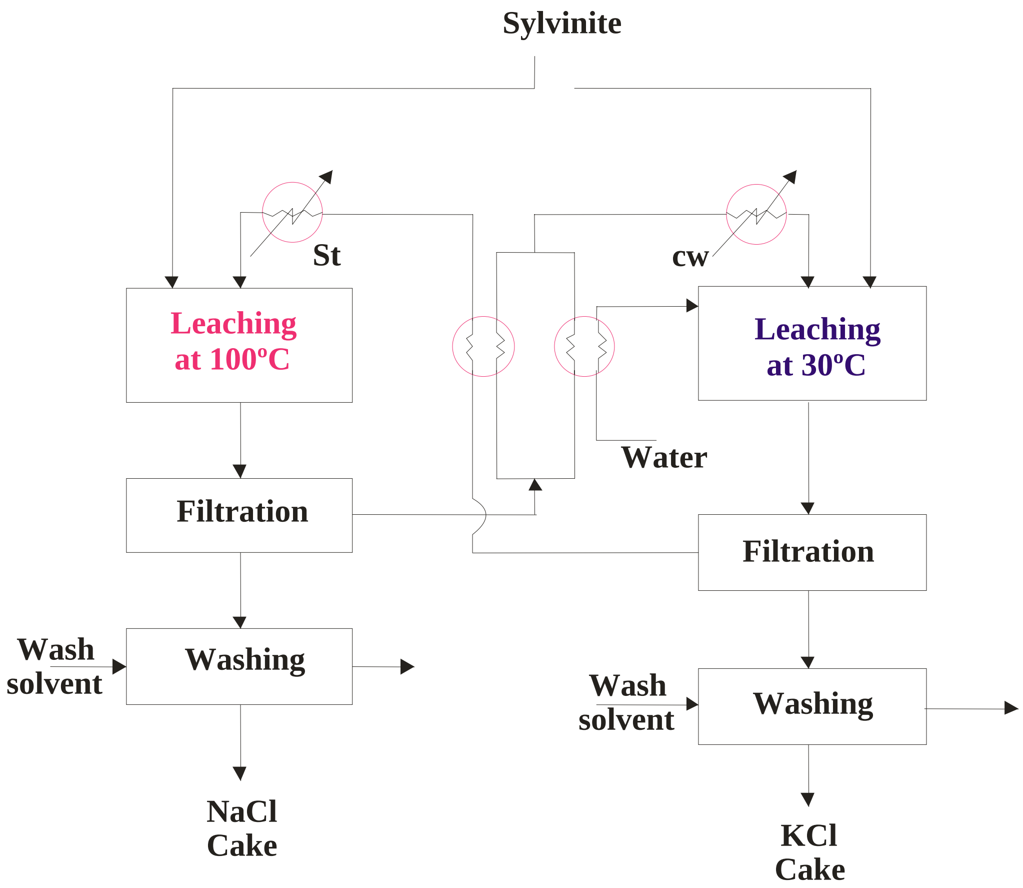
Objective Function

objective function minimizes the total venture cost:

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

Example: Sylvinite

The MILP formulation contains 299 equations, 218 continuous variables, and 27 binary variables.



Sylvinite.gms
Sylvinite_heat.gms
Sylvinite_wash.gms
Sylvinite_wash_heat.gms

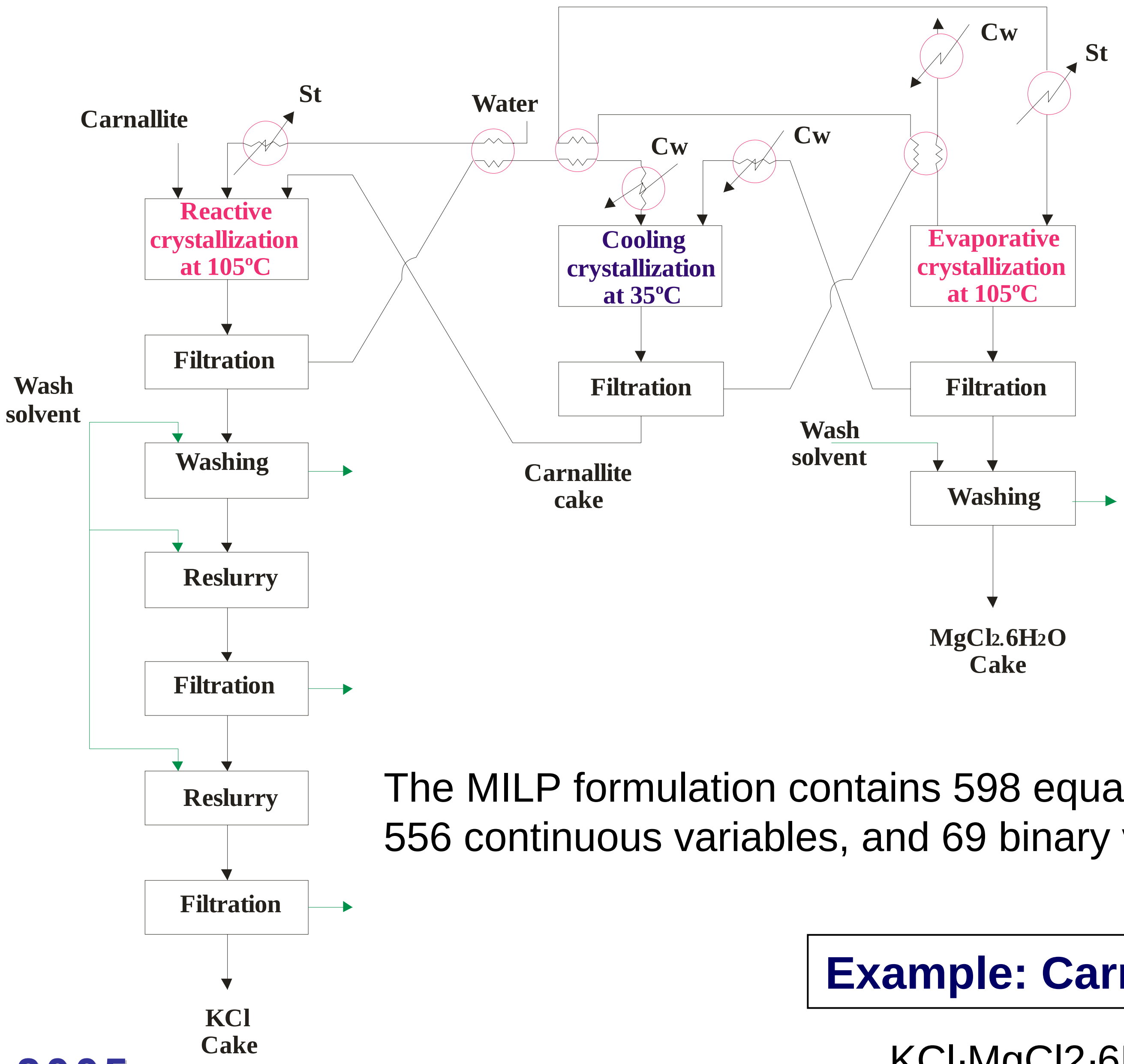
Examples-Carnallite

Production of potassium chloride and magnesium chloride from carnallite ($KCl.MgCl_2.6H_2O$).

Equilibrium Data

key	Temperature [°C]	Weight Composition		Solid Phase
		KCl	$MgCl_2$	
C1	35	3.8	27.32	KCl+Carnallite
C2	35	0.14	35.17	Carnallite+$MgCl_2.6H_2O$
H1	105	7	30.82	KCl+Carnallite
H2	105	1.07	40.75	Carnallite+$MgCl_2.6H_2O$

Fractional Crystallization with Heat Integration & Cake Washing

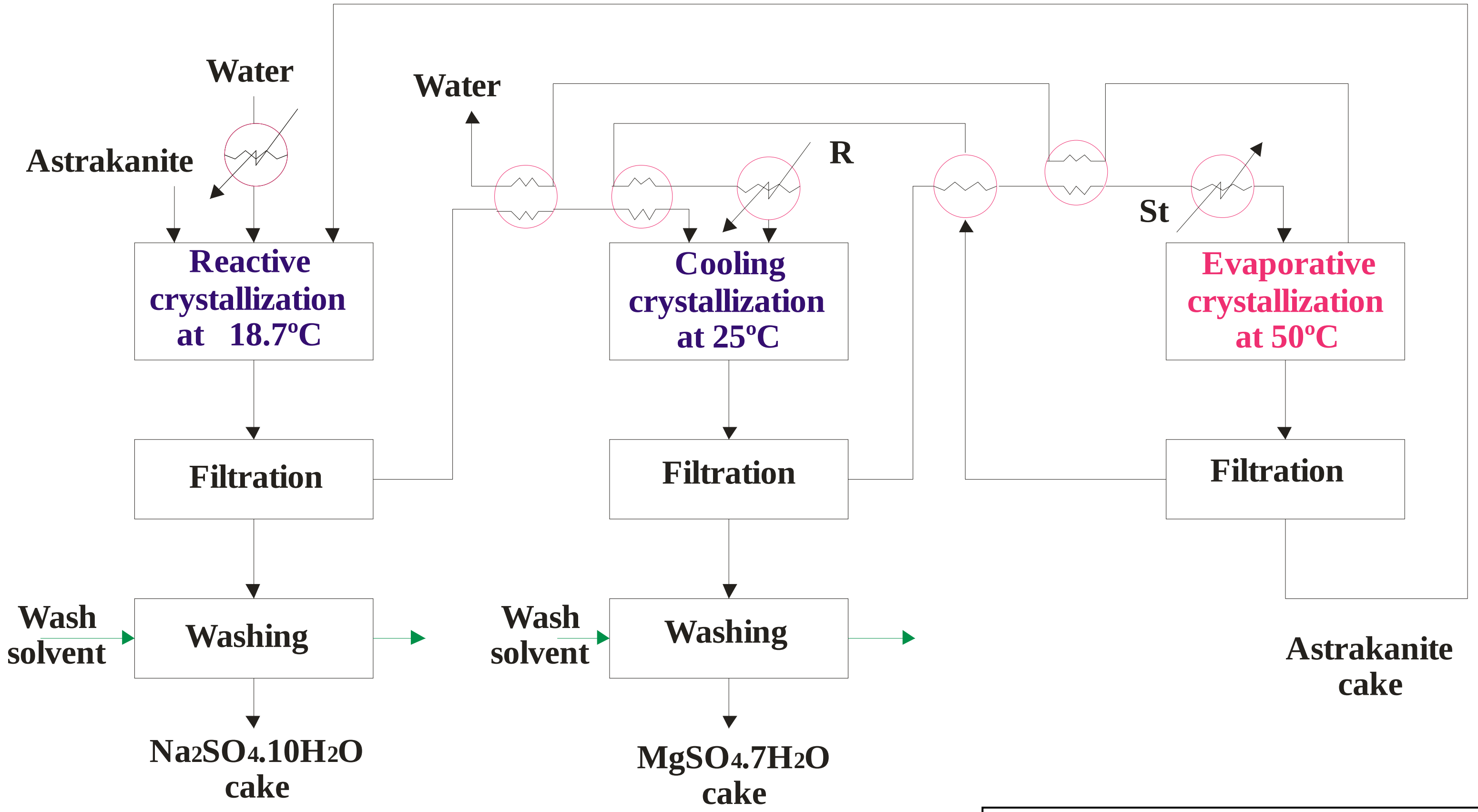


The MILP formulation contains 598 equations, 556 continuous variables, and 69 binary variables

Example: Carnallite

KCl·MgCl2·6H2O

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.



Example: Astrakanite

$MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$

Final Remark

- Complete examples
- Complete list of references on design of separation based on crystallization (metathetical salts, drowning-out, reactive crystallization, wastewater systems, chiral crystallization)
- Other papers
- Links

Can be found on

http://www.ingen.uantof.cl/webpages/Academicos%20Ing.%20Quimica/Luiscisternas/principal.htm

Or

http://cepac.cheme.cmu.edu/pasifaculty.htm

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