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MODELING OF MULTISTAGE SALT CRYSTALLIZATION FROM THE NaCl–Na₂SO₄–H₂O SYSTEM

A three-component system and the crystallization of selected salts from this system were investigated in this study. The studied system was a NaCl–Na₂SO₄–H₂O three-component solution. A methodology for selective crystallization by various elementary pathways was developed, followed by a mathematical model of the complex process of selective crystallization. The developed mathematical model and algorithm of the process enabled the simulation of selective salt crystallization from the multicomponent system NaCl–Na₂SO₄–H₂O.

Key words: NaCl–Na₂SO₄–H₂O System, Crystallization of selected salts from multicomponent systems, Modeling, Simulation.

The design and simulation of a chemical–technological system is a complex task, the solution of which began with the appearance of computers. The first program for calculating the balance of a complex chemical process appeared in 1958. Real progress in the number and quality of programs was recorded only in the last decades of the twentieth century.

The balancing of chemical processes and equipment involves a group of activities that are performed in order to determine the relevant parameters of all the process lines and the material and energy consumption for process operation.

The synthesis of a crystallization, regardless of whether it is isothermal or non–isothermal, is a relatively new field in the synthesis of chemical processes. Important results in the investigation of isothermal crystallizations were presented by A.W. Westerberg and J.B. Hillenbrand [1–3]. Methods of studying multi–stage evaporator units were presented in these papers, as well the method of choosing the optimal technological structure of the process and the determination of the optimal temperature regime in the evaporation unit.

Investigation of the selective salt crystallization from multicomponent systems originates from B. Fitch [4], who systematically presented a review of the various pathways of salt crystallization from four–component systems. Other authors that have studied the computer–aided crystallization [5–8] also referred to the results of this author. The cited references are also important because they significantly contributed to the synthesis of a crystallization, specifically from Na₂SO₄–K₂SO₄–H₂O and NaCl–KCl–H₂O systems.

The selective crystallization from a multicomponent NaCl–Na₂SO₄–H₂O system in order to obtain NaCl and Na₂SO₄ crystals was investigated in this study. A

methodology for selective crystallization by various methods (isothermal, adiabatic,...) was developed, which was followed by the development of a mathematical model of the complex process of selective crystallization. The developed mathematical model and algorithm for the calculation enabled the simulation of selective salt crystallization from the multicomponent system NaCl–Na₂SO₄–H₂O.

ALTERNATIVE WAYS OF SALT CRYSTALLIZATION FROM THREE–COMPONENT SYSTEMS

In order to fully describe the state of the three–component system, it is necessary to know the intensive and extensive phase parameters such as temperature, pressure, volume, enthalpy, component concentration in the individual phases, etc. The phase equilibrium in solutions does not depend on the amount of solution. Therefore, in order to describe the equilibrium, it is only necessary to know the intensive phase parameters such as temperature, pressure and the component concentration in each phase. The phase equilibrium in salt solutions are presented in the form of phase diagrams. The isothermal sections of the spacial diagram of the three–component systems of the AX–AY–H₂O type have the shape of a triangle.

Constitutive elements of technological structures

Selective fractional crystallization may be performed by one or a combination of several crystallization processes, which depends on the concentration of the feed, the requested product and various restrictions set by the process. The possible technological structures may have the following constitutive elements:

a) evaporation at constant temperature (isothermal evaporation)

b) crystallization at constant temperature (isothermal crystallization)

c) crystallization with a constant amount of water (cooling crystallization)

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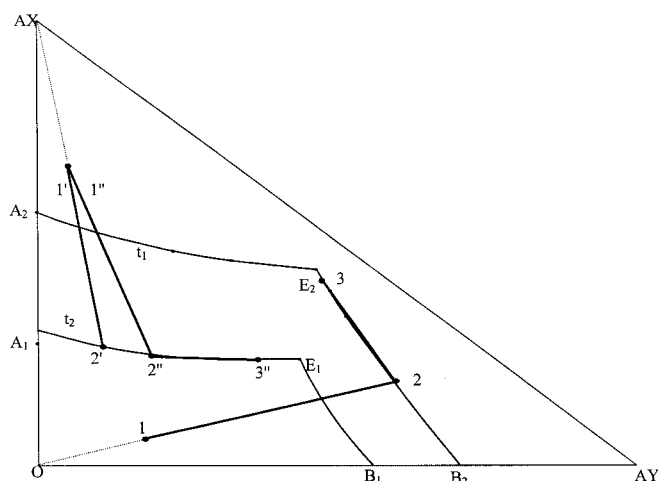


Figure 1. Trajectories of the basic crystallization processes in three-component systems without compounds formation

d) evaporation and crystallization without heat exchange (adiabatic crystallization).

The process of **isothermal evaporation** of water in AX–AY–H₂O three-component systems is presented by the line 1–2 (Figure 1). Since only water evaporates during evaporation, the ratio of the salts AX and AY does not change, so the trajectory of the evaporation moves along a straight line drawn through the coordinate beginning and the point which defines the concentration of the starting solution until it intersects with the isotherm saturation line at which evaporation occurs.

If evaporation continues at constant temperature, then of one of the dissolved salts is **crystallizing** and the point showing the composition of the solution moves along the saturation line. This process is presented by line 2–3 (Figure 1).

Isochrydic crystallization or crystallization by cooling the solution without water evaporation is presented in the phase diagram of the three-component system by the straight line 1'–2' (Figure 1).

If, however, the three-component solution is introduced into a crystallizer in which the pressure is considerably reduced, sudden boiling occurs until equilibrium is established between the pressure and vapor pressure. This process is called **adiabatic evaporation**. If the crystallization of one of the dissolved salts takes place at the same time, then this is **adiabatic crystallization**. The processes of adiabatic evaporation and crystallization are presented in the phase diagram by the lines 1''–2''–3'' (Figure 1).

Alternative pathways of selective salt crystallization from three-component systems

The synthesis of all the possible alternative processes of selective salt crystallization from three-component systems was derived on the basis of phase diagrams, literature data and the relationships between the intensive and extensive properties of the system. The equilibrium conditions and relationships in

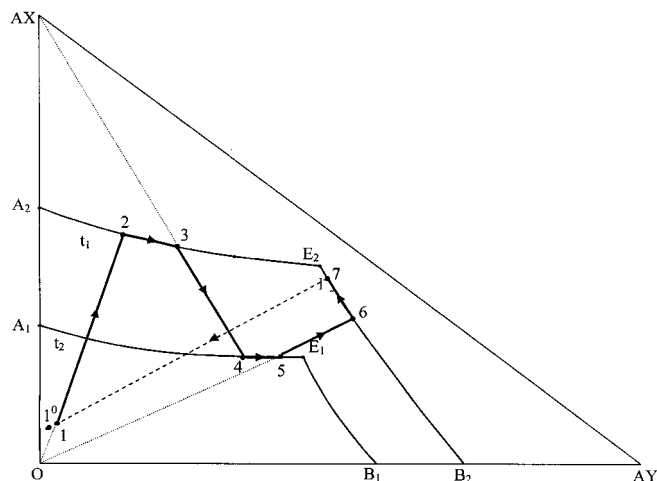


Figure 2. Trajectory of selective crystallization in a three-component system

the system had to be carefully defined for each specific case. The general principle: what is valid for the general case is also valid for individual cases, should be followed.

The phase diagram for the general three-component system AX–AY–H₂O with an appropriate isotherm, is presented in Figure 2. Depending on the location of the point representing the composition of the initial solution, it is possible to present different trajectories of selective salt crystallization from the given solution. All these different processes consist of a series of individual elementary processes that were discussed in the previous section and presented in Figure 1.

All the possible alternative ways of selective crystallization that may be synthesized and presented in the phase diagram will not be considered in this paper. However, one of the alternative ways is presented by points 1–7 (Figure 2). It consists of the following individual elementary steps: isothermal evaporation 1–3, adiabatic evaporation 3–5, isothermal evaporation 5–7 and mixing of the solution 7 with the initial solution 1°.

DEVELOPMENT OF A MATHEMATICAL MODEL OF SELECTIVE SALT CRYSTALLIZATION FROM THE THREE-COMPONENT SYSTEM NaCl–Na₂SO₄–H₂O

The three-component solution NaCl–Na₂SO₄–H₂O is obtained by the subterranean or surface extraction of the mineral halite and by removing the impurities that appear in the solution. This solution may contain various concentrations of the salts NaCl and Na₂SO₄. In this case the three-component system NaCl–Na₂SO₄–H₂O has the following mass fractions: about 0.25 of NaCl and 0.008 of Na₂SO₄. The synthesis of the selective crystallization of NaCl and Na₂SO₄ from this system is presented in the phase diagram (Figure 3). The technological scheme of the process is shown in Figure 4. The feed of the designated concentration presented by point 1 is heated to a temperature higher than 100°C. The heated solution is introduced into

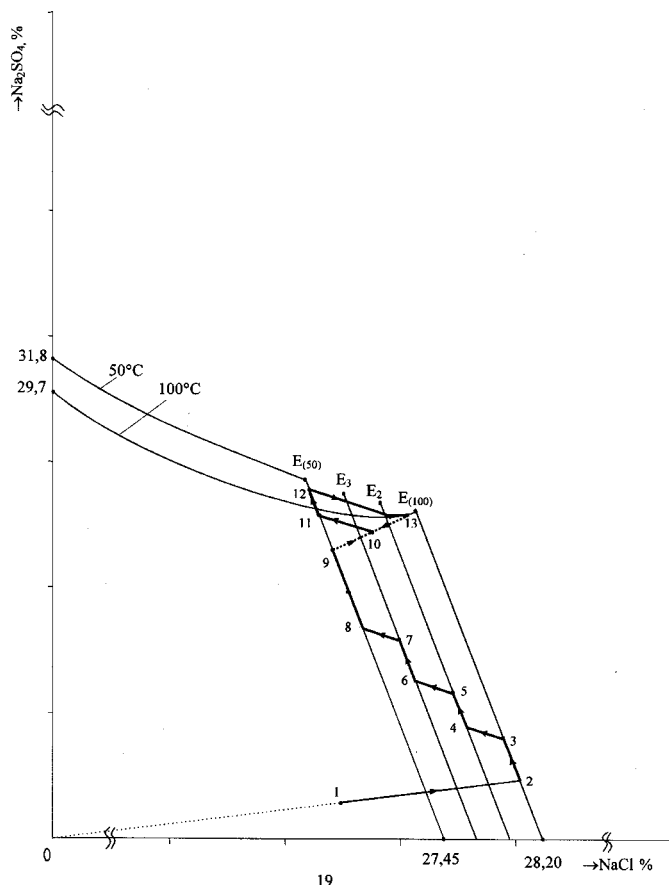
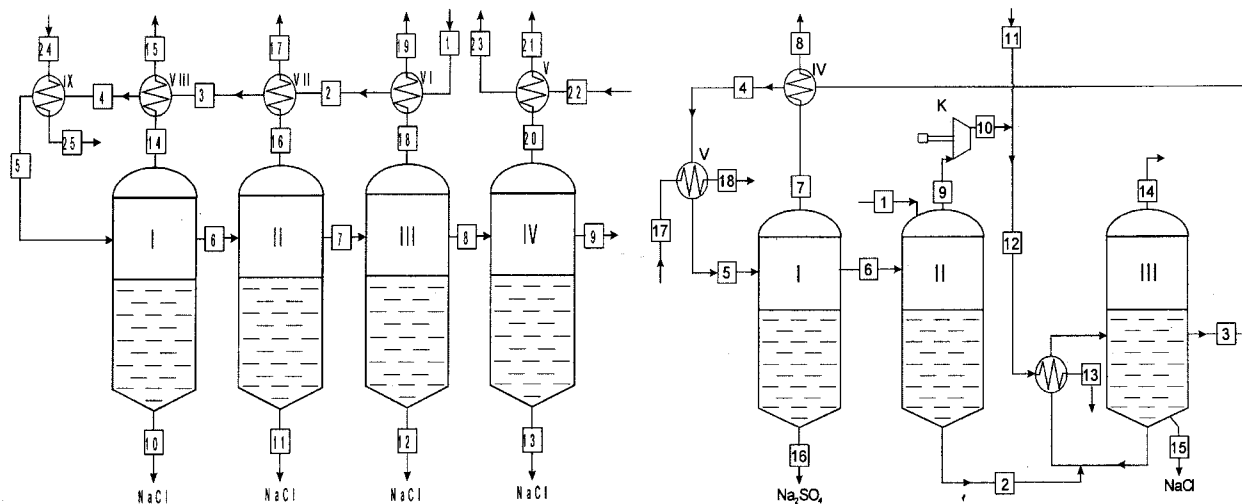


Figure 3. Trajectory of the selective salt crystallization in the system NaCl-Na₂SO₄-H₂O

evaporator-crystallizer I. The composition of the solution from crystallizer I corresponds to point 3. NaCl crystallizes in it, which is presented by the line 2-3. The solution from crystallizer I enters into crystallizer II and the solution leaving it has the composition designated by point 5. NaCl crystallizes along the line 4-5. The solution from crystallizer II enters crystallizer III and the composition of the solution leaving it is designated by point 7. The crystallization of NaCl occurs along the line 6-7. From crystallizer III the solution enters into crystallizer IV and the solution leaving it has the composition designated by point 9 and its temperature is 50°C. This solution, the concentration of which is close to the eutectic point, is transported to the unit for the fractional crystallization of NaCl and Na₂SO₄, which is also presented in Figure 4b.

The solution from the unit for evaporating the three-component solution, the composition of which is presented by point 9 (Figure 3), is mixed with the solution originating from the sodium sulphate crystallizer, the composition of which is designated by point 13. A mixed solution defined by point 10 is formed. This solution is expanded in the expansion vessel and subsequently NaCl crystallizes in the sodium chloride crystallizer as represented by the line 11-12. At the exit from the sodium chloride crystallizer the solution has the composition represented by point 12 and its temperature is 50°C. This solution is heated to a temperature higher than 100°C (usually to 140°C) and introduced into an adiabatic evaporator where the temperature is reduced to 100°C, and Na₂SO₄ crystallizes. The composition of the solution exiting the



a) Evaporation of the solution NaCl-Na₂SO₄-H₂O
 I,II,III,IV- adiabatic evaporators-crystallizers
 V,VI,VII,VIII,IX- condensers

b) The selective crystallization of NaCl and Na₂SO₄
 I- adiabatic evaporator-crystallizer
 II- expansion vessel
 III- isothermal evaporator-crystallizer
 IV- condenser; K- compressor
 V- preheater with fresh steam

Figure 4. ? Scheme of selective salt crystallization from the system NaCl-Na₂SO₄-H₂O

adiabatic evaporator corresponds to point 13. This solution is mixed with the solution from the evaporating unit (as previously described) and thus the cycle is closed.

Development of a mathematical model of the evaporation of a NaCl–Na₂SO₄–H₂O solution

The evaporation of the NaCl–Na₂SO₄–H₂O solution presented in the technological scheme (Figure 4) has designations of flow lines, the parameters of which need to be determined by solving the mass and energy balances. The mass and energy balance of the total process and each steps unit individually is described by a system of 71 algebraic equations with the following designations:

j – designation of flow the line ($j=1...25$)

G_j – flow rate of line j (kg/h)

c_{id}^j – mass fraction of component [$i=1$ (NaCl) and 2 (Na₂SO₄) in the flow line j]

h_j – specific enthalpy of line j (kJ/kg)

t_j – temperature of line j (°C)

q_{km} – enthalpy of crystallization in the m -th crystallizer ($m=1...4$)

p_m – pressure in the crystallizer ($m=1...4$)

a_w – water activity in the solution

p_j^w – water vapour pressure of pure water at the temperature of the j -th flow line

The system of algebraic equations has 71 equations:

$$G_1 - G_6 - G_{10} - G_{14} = 0 \quad (f1)$$

$$G_1 c_1^{(1)} - G_6 c_1^{(6)} - G_{10} c_1^{(10)} = 0 \quad (f2)$$

$$G_1 c_2^{(1)} - G_6 c_2^{(6)} = 0 \quad (f3)$$

$$c_2^{(6)} = f(t_6, c_1^{(6)}) \quad (f4)$$

$$p_1 = a_{w6} \cdot p_6^w \quad (f5)$$

$$a_{w6} = f(t_6, c_1^{(6)}, c_2^{(6)}) \quad (f6)$$

$$p_6^w = f(t_6) \quad (f7)$$

$$h_1 = f(t_1, c_1^{(1)}, c_2^{(1)}) \quad (f8)$$

$$h_2 = f(t_2, c_1^{(1)}, c_2^{(1)}) \quad (f9)$$

$$h_3 = f(t_3, c_1^{(1)}, c_2^{(1)}) \quad (f10)$$

$$h_4 = f(t_4, c_1^{(1)}, c_2^{(1)}) \quad (f11)$$

$$h_5 = f(t_5, c_1^{(1)}, c_2^{(1)}) \quad (f12)$$

$$h_{14} = f(t_6, p_1) \quad (f13)$$

$$h_{10} = f(t_6, c_1^{(10)}) \quad (f14)$$

$$q_{k1} = f(t_6, c_1^{(6)}, c_2^{(6)}) \quad (f15)$$

$$G_{14} (h_{14} - h_{15}) = G_1 (h_4 - h_3) \quad (f16)$$

$$h_{15} = f(p_1) \quad (f17)$$

$$G_{24} (h_{24} - h_{25}) = G_1 (h_5 - h_4) \quad (f18)$$

$$h_{24} = f(t_{24}) \quad (f19)$$

$$h_{25} = f(t_{24}) \quad (f2)$$

$$t_{14} = t_6 \quad (f21)$$

$$G_1 h_5 - G_6 h_6 - G_{10} h_{10} - G_{14} h_{14} + G_{10} q_{k1} = 0 \quad (f22)$$

$$d_{t1} = t_6 - t_4 \quad (f23)$$

$$G_6 - G_7 - G_{11} - G_{16} = 0 \quad (f24)$$

$$G_6 c_1^{(6)} - G_7 c_1^{(7)} - G_{11} c_1^{(11)} = 0 \quad (f25)$$

$$G_6 c_2^{(6)} - G_7 c_2^{(7)} = 0 \quad (f26)$$

$$c_2^{(7)} = f(t_7, c_1^{(7)}) \quad (f27)$$

$$p_2 = a_{w7} \cdot p_7^w \quad (f28)$$

$$a_{w7} = f(t_7, c_1^{(7)}, c_2^{(7)}) \quad (f29)$$

$$p_7^w = f(t_7) \quad (f30)$$

$$h_7 = f(t_7, c_1^{(7)}, c_2^{(7)}) \quad (f31)$$

$$h_{11} = f(t_7, c_1^{(11)}) \quad (f32)$$

$$q_{k2} = f(t_7, c_1^{(11)}, c_2^{(11)}) \quad (f33)$$

$$h_{16} = f(t_7, p_2) \quad (f34)$$

$$h_{17} = f(p_2) \quad (f35)$$

$$t_{16} = t_7 \quad (f36)$$

$$G_{16} (h_{16} - h_{17}) = G_1 (h_3 - h_2) \quad (f37)$$

$$G_6 h_6 - G_7 h_7 - G_{11} h_{11} - G_{16} h_{16} + G_{11} q_{k2} = 0 \quad (f38)$$

$$G_7 - G_8 - G_{12} - G_{18} = 0 \quad (f39)$$

$$G_7 c_1^{(7)} - G_8 c_1^{(8)} - G_{12} c_1^{(12)} = 0 \quad (f40)$$

$$G_7 c_2^{(7)} - G_8 c_2^{(8)} = 0 \quad (f41)$$

$$c_2^{(8)} = f(t_8, c_1^{(8)}) \quad (f42)$$

$$p_3 = a_{w8} \cdot p_8^w \quad (f43)$$

$$a_{w8} = f(t_8, c_1^{(8)}, c_2^{(8)}) \quad (f44)$$

$$p_8^w = f(t_8) \quad (f45)$$

$$h_8 = f(t_8, c_1^{(8)}, c_2^{(8)}) \quad (f46)$$

$$h_{12} = f(t_8, c_1^{(12)}) \quad (f47)$$

$$q_{k3} = f(t_8, c_1^{(8)}, c_2^{(8)}) \quad (f48)$$

$$h_{18} = f(t_8, p_3) \quad (f49)$$

$$h_{19} = f(p_3) \quad (f50)$$

$$t_{18} = t_8 \quad (f51)$$

$$G_{18} (h_{18} - h_{19}) = G_1 (h_2 - h_1) \quad (f52)$$

$$G_7 h_7 - G_8 h_8 - G_{12} h_{12} - G_{18} h_{18} + G_{12} q_{k3} = 0 \quad (f53)$$

$$G_8 - G_9 - G_{13} - G_{20} = 0 \quad (f54)$$

$$G_8 c_1^{(8)} - G_9 c_1^{(9)} - G_{13} c_1^{(13)} = 0 \quad (f55)$$

$$G_8 c_2^{(8)} - G_9 c_2^{(9)} = 0 \quad (f56)$$

$$c_2^{(9)} = f(t_8, c_1^{(9)}) \quad (f57)$$

$$p_4 = a_{w9} \cdot p_9^w \quad (f58)$$

$$a_{w9} = f(t_9, c_1^{(9)}, c_2^{(9)}) \quad (f59)$$

$$p_9^w = f(t_9) \quad (f60)$$

$$h_9 = f(t_9, c_1^{(9)}, c_2^{(9)}) \quad (f61)$$

$$h_{13} = f(t_9, c_1^{(13)}) \quad (f62)$$

$$h_{20} = f(t_9, p_4) \quad (f63)$$

$$t_{20} = t_9 \quad (f64)$$

$$h_{21} = f(p_4) \quad (f65)$$

$$h_{22} = f(t_{22}) \quad (f66)$$

$$h_{23} = f(t_{23}) \quad (f67)$$

$$G_{20}(h_{20} - h_{21}) = G_{22}(h_{23} - h_{22}) \quad (f68)$$

$$G_8 h_8 - G_9 h_9 - G_{13} h_{13} - G_{20} h_{20} + G_{13} q_{k4} = 0 \quad (f69)$$

$$g_{k4} = f(t_9, c_1^{(9)}, c_2^{(9)}) \quad (f70)$$

$$g_6 = f(t_6, c_1^{(6)}, c_2^{(6)}) \quad (f71)$$

The number of degrees of freedom of this system of 71 equations with 83 variables is:

$$S = 83 - 71 = 12$$

Therefore, the group of free variables should be 12 variables. This group consists of the following variables:

- the flow rate of the feed, G_1
- the NaCl content in the feed, $c_1^{(1)}$
- the Na_2SO_4 content in the feed, $c_1^{(2)}$
- the Na_2SO_4 content at the exit from adiabatic evaporator I, $c_2^{(6)}$
- the temperature of the solution from adiabatic evaporator I, t_6
- the temperature of the solution from adiabatic evaporator II, t_7
- the temperature of the solution from adiabatic evaporator III, t_8
- the temperature of the solution from adiabatic evaporator IV, t_9
- the useful minimal temperature difference, d_{11}
- the cooling water temperature at the entrance to condenser V, t_{22}
- the cooling water temperature at the exit from condenser V, t_{23}
- the temperature of fresh dry saturated steam, t_{24} .

A mathematical model, presented by the corresponding algorithm in Figure 5, was developed for this system of equations and group of free variables. This algorithm – flow diagram presents the solution of the system of balance equations for a four-stage adiabatic plant for evaporating the $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$ solution presented in Figure 4.

Development of a mathematical model for the selective crystallization of NaCl and Na_2SO_4

The selective crystallization of NaCl and Na_2SO_4 presented in the technological scheme (Figure 4) has designations of flow lines, the parameters of which must be determined by solving the mass and energy balance.

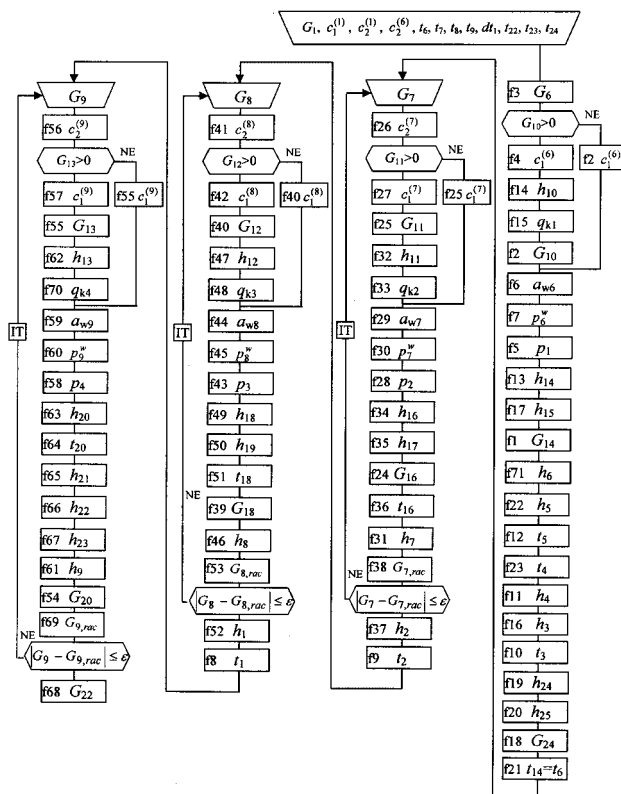


Figure 5. Flow diagram – algorithm for solving a system of balance equations of a four-stage adiabatic evaporation of the system $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$

The mass and energy balance of the total process and each individual process unit is described by a system of algebraic equations that consists of 56 equations in which the designations have the same meaning as in the previous case.

$$G_3 - G_6 - G_7 - G_{16} = 0 \quad (f1)$$

$$G_3 c_2^{(3)} - G_6 c_2^{(6)} - G_{16} c_2^{(16)} \quad (f2)$$

$$G_3 c_1^{(3)} - G_6 c_1^{(6)} = 0 \quad (f3)$$

$$c_1^{(6)} = f(t_6, c_2^{(6)}) \quad (f4)$$

$$p_1 = a_{w6} \cdot p_6^w \quad (f5)$$

$$a_{w6} = f(t_6, c_1^{(6)}, c_2^{(6)}) \quad (f6)$$

$$p_6^w = f(t_6) \quad (f7)$$

$$h_5 = f(t_5, c_1^{(3)}, c_2^{(3)}) \quad (f8)$$

$$h_6 = f(t_6, c_1^{(6)}, c_2^{(6)}) \quad (f9)$$

$$h_7 = f(t_6, p_1) \quad (f10)$$

$$h_{16} = f(t_6, c_2^{(16)}) \quad (f11)$$

$$q_{k1} = f(t_6, c_1^{(6)}, c_2^{(6)}) \quad (f12)$$

$$G_7 (h_7 - h_8) = G_3 (h_4 - h_3) \quad (f13)$$

$$h_8 = f(p_1) \quad (f14)$$

$$G_{17} (h_{17} - h_{18}) = G_3 (h_5 - h_4) \quad (f15)$$

$$h_{17} = f(p) \quad (f16)$$

$$h_4 = f(t_4, c_1^{(3)}, c_2^{(3)}) \quad (f17)$$

$$h_{18} = f(p) \quad (f18)$$

$$G_3 h_5 - G_6 h_6 - G_7 h_7 - G_{16} h_{16} + G_{16} q_{k1} = 0 \quad (f19)$$

$$dt_1 = t_6 - t_4 \quad (f20)$$

$$G_1 + G_6 - G_2 - G_9 = 0 \quad (f21)$$

$$G_1 c_1^{(1)} + G_6 c_1^{(6)} - G_2 c_1^{(2)} = 0 \quad (f22)$$

$$G_1 c_2^{(1)} + G_6 c_2^{(6)} - G_2 c_2^{(2)} = 0 \quad (f23)$$

$$p_2 = a_{w2} \cdot p_2^w \quad (f24)$$

$$a_{w2} = f(t_2, c_1^{(2)}, c_2^{(2)}) \quad (f2)$$

$$p_2^w = f(t_2) \quad (f2)$$

$$h_1 = f(t_1, c_1^{(1)}, c_2^{(1)}) \quad (f2)$$

$$h_2 = f(t_2, c_1^{(2)}, c_2^{(2)}) \quad (f2)$$

$$h_9 = f(t_2, p_2) \quad (f2)$$

$$h_{10} = h_{12} \quad (f30)$$

$$h_{11} = h_{12} \quad (f31)$$

$$h_{12} = f(p) \quad (f32)$$

$$P_k = G_9 (h_c - h_9) \quad (f33)$$

$$h_c = h_9 + \frac{h_s - h_9}{\eta} \quad (f34)$$

$$h_s = f(p, p_2, t_2) \quad (f35)$$

$$G_{12} - G_{11} - G_{10} = 0 \quad (f36)$$

$$G_9 + G_k - G_{10} = 0 \quad (f37)$$

$$G_9 h_c + G_k h_{13} - G_{10} h_{10} = 0 \quad (f38)$$

$$G_k = G_9 \frac{h_c - h_{10}}{h_{10} - h_{13}} \quad (f39)$$

$$Q_{tr} = G_{12} (h_{12} - h_{13}) \quad (f40)$$

$$h_{13} = f(p) \quad (f41)$$

$$dt_{min} = t_{12} - t_3 \quad (f42)$$

$$G_6 h_6 + G_1 h_1 - G_2 h_2 - G_9 h_9 = 0 \quad (f43)$$

$$t_{12} = f(p) \quad (f44)$$

$$G_2 - G_3 - G_{14} - G_{15} = 0 \quad (f45)$$

$$G_2 c_1^{(2)} - G_3 c_1^{(3)} - G_{15} c_1^{(15)} = 0 \quad (f46)$$

$$G_2 c_2^{(2)} - G_3 c_2^{(3)} = 0 \quad (f47)$$

$$c_2^{(3)} = f(t_3, c_1^{(3)}) \quad (f48)$$

$$p_3 = a_{w3} \cdot p_3^w \quad (f49)$$

$$a_{w3} = f(t_3, c_1^{(3)}, c_2^{(3)}) \quad (f50)$$

$$p_3^w = f(t_3) \quad (f51)$$

$$h_3 = f(t_3, c_1^{(3)}, c_2^{(3)}) \quad (f52)$$

$$h_{14} = f(t_3, p_3) \quad (f53)$$

$$h_{15} = f(t_3, c_1^{(15)}) \quad (f54)$$

$$q_{k3} = f(t_3, c_1^{(3)}, c_2^{(3)}) \quad (f55)$$

$$Q_{tr} + G_2 h_2 - G_3 h_3 - G_{14} h_{14} - G_{15} h_{15} + G_{15} q_{k3} = 0 \quad (f56)$$

The number of degrees of freedom for this system of 56 equations and 66 variables is:

$$S = 66 - 56 = 10$$

The number of degrees of freedom indicates that the group of free variables should be previously assigned 10 variables. This group may consist of:

- the flow rate of the flow line coming from the evaporation unit, $G_1 = G_9$
- the flow rate of fresh water vapor, G_{11}
- the NaCl content in the feed, $c_1^{(1)}$
- the Na_2SO_4 content in the feed, $c_2^{(1)}$
- the NaCl content in the flow line from the adiabatic evaporator, $c_1^{(6)}$
- the temperature of the flow line, t_1
- the temperature of the flow line, t_2
- the temperature of the flow line, t_6
- pressure, p
- the flow rate of the solution coming out of the adiabatic evaporator, G_6 .

The mathematical model presented in Figure 6 was developed for this system of equations and group of free variables. This algorithm – flow diagram presents the solution of the system of balance equations of the process of selective crystallization of NaCl and Na_2SO_4 from the concentrated NaCl– Na_2SO_4 – H_2O solution presented in the technological scheme (Figure 4).

Simulation of the evaporation of a three-component NaCl– Na_2SO_4 – H_2O solution and the selective crystallization of NaCl and Na_2SO_4

The developed mathematical models, presented in the previous sections of this paper, prove their functionality and correctness by the simulation – calculation of the basic variables of all the flow lines presented in the process scheme for defined values of the free variables. In the given example the group of initial process variables consists of ($G_1, c_1^{(1)}, c_2^{(1)}, c_2^{(6)}, t_6, t_7, t_8, t_9, dt_1, t_{22}, t_{23}, t_{24}$). If these variables are assigned the values (10000; 0.2497; 0.0083; 0.0093; 110; 95; 85; 50; 10; 20; 35; 184), the values for all the other parameters of the flow lines presented in the technological scheme (Figure 4) are calculated by the mathematical model simulation.

In the same manner, the group of initial variables for the selective crystallization of NaCl and Na_2SO_4 (Figure 4) designated as ($G_1; G_{11}; t_1; t_2; t_6; p; c_1^{(1)}; c_2^{(1)}; c_1^{(6)}$) were substituted by the values (7399; 2933; 50; 63; 100; 11; 0.262; 0.0112; 0.2554). All the other variables of the flow lines presented in the denoted scheme may be calculated by solving the mathematical model.

The influence of the flow rate of the feed G_1 on the other process variables of the evaporation of the three-component solution NaCl– Na_2SO_4 – H_2O was

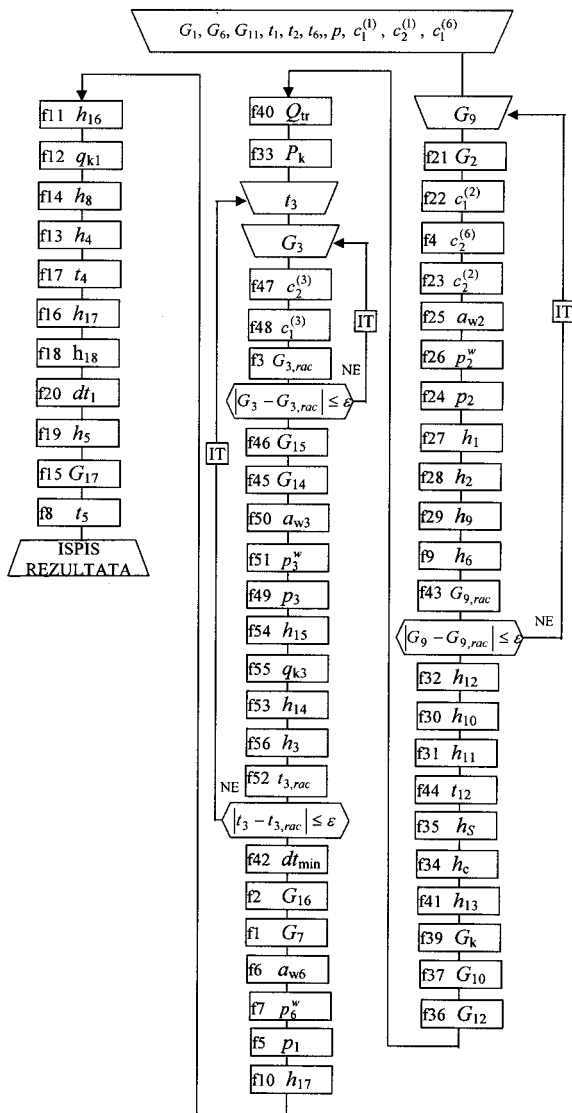


Figure 6. Flow diagram – algorithm for solving a system of balance equations for a unit for separating NaCl from Na₂SO₄

investigated. The corresponding characteristic data are presented in Tables 1 and 2.

As may be seen from Table 2, the consumption of fresh steam G_{24} is proportional to the flow rate of the feed, while the consumption of fresh steam per unit mass of evaporated water is approximately constant for a defined temperature and solution concentration.

The influence of temperature t_6 and flow rate G_1 on the other variables of the selective crystallization of NaCl and Na₂SO₄ was also investigated. The corresponding characteristic data are presented in Tables 3 and 4.

Analysis of the results presented in Table 3 indicates that the technological structure of the process at $t_6 = 100^\circ\text{C}$ and $t_6 = 110^\circ\text{C}$ is unreal because in practice it is not possible to reach such high vacuum that would correspond to the calculated values of temperature t_3 . Under real conditions the temperature t_3

Table 1. Influence of the flow rate of the feed G_1 on the component mass flow

G_1 (kg/h)	G_6 (kg/h)	G_7 (kg/h)	G_8 (kg/h)	G_9 (kg/h)	G_{10} (kg/h)	G_{11} (kg/h)	G_{12} (kg/h)	G_{13} (kg/h)
7000	6247	5967	5756	5176	16.4	106.4	87.2	181.3
8000	7140	6820	6580	5918	18.8	121.4	99.4	207
9000	8032	7673	7403	6658	21.1	136.5	111.8	233
10000	8924	8526	8226	7399	23.5	151.5	124.2	258.6
11000	9817	9379	9050	8140	25.8	166.6	136.4	284.6
12000	10710	10232	9873	8880	28.2	181.6	148.8	310.5
13000	11602	11085	10697	9622	30.5	196.7	161	336

Table 2. Influence of the flow rate of the feed G_1 on the consumption of fresh steam and the amount of evaporated water

G_1 (kg/h)	7000	8000	9000	10000	11000	12000	13000
G_{24} (kg/h)	967.5	1105.7	1243.9	1382.1	1520.3	1658.6	1796.8
evaporated water (kg/h)	1432.7	1635.4	1839.6	2039.9	2246.6	2450.9	2653.8
kg of evaporated water r/kg steam	1.481	1.479	1.479	1.478	1.478	1.477	1.477

is 50°C . The temperature range of t_6 between 120°C and 130°C is realistic. With increasing temperature t_6 , the temperature of the solution after crystallization t_3 increases, the consumption of fresh steam decreases and the compressor power increases.

The values presented in Table 4 show that the consumption of fresh steam G_{17} and the temperature of the solution t_3 increase with increasing flow rate of the feed G_1 , while the compressor power P decreases. Obviously flow rate G_1 cannot be arbitrarily high because it is limited by the real interval of temperature t_3 . For higher values of the flow rate G_1 , the consumption of fresh steam G_{11} should be increased.

Table 3. Influence of the temperature of the solution t_6 on the mass balance parameters

t_6 °C	G_2 (kg/h)	G_3 (kg/h)	G_{16} (kg/h)	G_{15} (kg/h)	G_{17} (kg/h)
100	16599	10003	85.5	2005	1585.8
110	16461	9987	85.5	2005	1531.1
120	16303	9987	85.5	2005	1432.2
130	16144	9987	85.5	2005	1329.2

Table 4. Influence of the flow rate of the feed G_1 on the mass balance parameters

G_1 (kg/h)	G_2 (kg/h)	G_3 (kg/h)	G_{16} (kg/h)	G_{15} (kg/h)	G_{17} (kg/h)	t_3 °C	P (kW)
5176	14108	9930	58.0	1360.7	214.4	87	765.1
5918	14865	9947	66.3	1555.2	681.5	62	740.1
6658	15621	9964	74.6	1749.2	1113.9	40	713.5
7399	16599	9987	85.5	2005	1585.8	16	680.2

CONCLUSION

A three-component chemical-technological system and the crystallization of selected salts from this system were investigated. Each crystallization process consists of constitutive elements, the trajectories of which are presented in the equilibrium phase diagram of three-component systems. In order to be able to practically apply the results of this study, a mathematical model was developed, the degrees of freedom determined, the starting variables defined and an algorithm – flow diagram for solving balance equations of the selective crystallization of salts from a three-component NaCl–Na₂SO₄–H₂O system developed. A technological scheme of the process was synthesized and it consisted of:

– a multistage unit for the adiabatic crystallization of NaCl,

– a combined isothermal and adiabatic unit for the selective crystallization of NaCl and Na₂SO₄.

The developed mathematical model enables the simulation of the process and investigation of all the balance variables for each flow line designated in the technological scheme of unit.

The results obtained by the simulation indicate the interdependence of the analyzed variables, of which only a few were discussed.

The choice of optimal input variables was enabled by investigating the selective crystallization of NaCl and Na₂SO₄ from a three-component system. The values of the balance variables characterizing the flow lines presented in the technological scheme were calculated.

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IZVOD

MODELOVANJE VIŠESTEPENE KRISTALIZACIJE SOLI IZ SISTEMA NaCl–Na₂SO₄–H₂O

(Naučni rad)

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U ovom radu proučavan je trokomponentni sistem koji je od značaja u tehnologiji neorganskih soli i kristalizacija selektovanih soli iz ovog sistema. Proučavani sistem je trokomponentni rastvor NaCl–Na₂SO₄–H₂O. Razvijena je metodologija selektivne kristalizacije različitim elementarnim putevima a zatim je razvijen matematički model složenog postupka selektivne kristalizacije. Razvijeni matematički model i algoritam ovog postupka omogućava simulaciju procesa selektivne kristalizacije soli iz višekomponentnog sistema NaCl–Na₂SO₄–H₂O. Opšte postavke razvijene u ovom radu su provjerenе simulacijom postupka selektivne kristalizacije soli iz sistema NaCl–Na₂SO₄–H₂O. Struktura postrojenja za selektivnu kristalizaciju soli iz ovog višekomponentnog sistema sastoji se od:

- višestepenog postrojenja za adijabatsku kristalizaciju NaCl,
 - kombinovanog izoternog i adijabatskog postrojenja za selektivnu kristalizaciju NaCl i Na₂SO₄.
- Simulacijom postupka dobijeni su rezultati koji omogućavaju izvođenje zavisnosti sledećih veličina:
- zavisnost protoka matičnog luga I, II, III i IV isparivača od protoka ulaznog rastvora je linearan,
 - količina isparene vode opada a potrošnja svježe pare po jedinici isparene vode raste.

Istraživanje postupka selektivne kristalizacije soli iz sistema NaCl–Na₂SO₄–H₂O i odgovarajuće funkcionalne zavisnosti omogućavaju izbor optimalnih ulaznih promjenljivih veličina i izračunavanje svih ostalih veličina koje karakterišu tokove označene na tehnološkoj šemi.

Ključne reči: Sistem NaCl–Na₂SO₄–H₂O • Kristalizacija selektovanih soli iz višekomponentnih sistema • Modelovanje • Simulacija •