

DELFT UNIVERSITY OF TECHNOLOGY

EQUIPMENT FOR HEAT AND MASS TRANSFER
ME45165

Equipment for Mass Transfer - Assignment 1

Crystallization

Authors

Group - Heat Transfer 12

Aswin Raghunathan (5128188)
Shyam Sundar Hemamalini (5071984)

March 16, 2020



Problem 1

Recovery of Potassium Nitrate from an Anthraquinone Dye Alkali Wastewater by Crystallization

1 Problem Description

In an industrial production plant, a KNO_3 containing water stream is discharged. It is required to design a crystallization process for the recovery of KNO_3 from this waste stream.

1.1 Outline

Prior to the design, a Mixed Suspension Mixed Product Removal (MSMPR) experiment was performed to estimate the kinetic parameters of crystallization using the given residence time τ_{exp} . The data from the experiment can be used to determine the crystal growth rate, nucleation rate and mean crystal size. Using this data and the solubility of KNO_3 in water, initial design decisions can be made by choosing appropriate crystallization method and mode of operation. Furthermore, the properties and composition at the inlet and outlet of the stream can be determined using a mass balance and displayed in the process flow sheet. The required heat capacity and the area for heat exchange can be determined using an energy balance. Finally, the geometric parameters of the crystallizer are estimated to fulfil the final design requirement.

1.2 Given Properties

The given physical properties, operating conditions of the feed and the chemical composition of the streams are tabulated below.

Parameters	Symbols	Units	Values
Weight Fraction of KNO_3 in solution	w_{feed}	wt%	35
Liquid Fraction in solution	ϵ	-	0.95
Feed Flow Rate	$\phi_{\text{v,feed}}$	m^3/hr	40
Residence Time	τ_{exp}	s	16000
Crystal Density	ρ_{cr}	kg/m^3	2100
Water Density	ρ_{water}	kg/m^3	1000
$\text{KNO}_3 - \text{H}_2\text{O}$ Solution Density	ρ_{sol}	kg/m^3	1250
Vapor Density	ρ_{vap}	kg/m^3	3
Solution Dynamic Viscosity	μ_{sol}	mPa s	0.885
Heat of Crystallization	ΔH_{cr}	J/mol	0
Heat of Evaporation	ΔH_{evap}	kJ/kg	1443
Specific Heat of Saturated Liquid	$C_{p,\text{liquid}}$	$\text{kJ}/\text{kg}/^\circ\text{C}$	3.11
Specific Heat of Saturated Crystals	$C_{p,\text{crystal}}$	$\text{kJ}/\text{kg}/^\circ\text{C}$	0.32

Table 1: Given properties

2 MSMPR Crystallization Model

From the MSMPR experiment data, the growth rate, nucleation rate and mean crystal size can be determined as per [1]. Equation 1 relates the population density of the particles with size $n(L)$ to the population density of the particles with size zero (n^0), growth rate (G) and residence time (τ). By taking the natural logarithm on both sides, we get equation 2 where the slope and intercept are obtained as $p_1 = -2888$ and $p_2 = 19.25$ respectively from the fitted curve as shown in figure 1.

$$n = n^0 \exp\left(\frac{-L}{G\tau}\right) \quad (1)$$

$$\ln(n) = \ln(n^0) + \left(\frac{-L}{G\tau} \right) = p_1 x + p_2 \quad (2)$$

The crystal growth rate, nucleation rate and mean crystal length can be determined from the equations 3, 4 and 5 respectively.

$$G = -\frac{1}{p_1 \tau} \quad (3)$$

$$B = n_0 G = \exp(p_2) G \quad (4)$$

$$L_{\text{mean}} = 4G\tau \quad (5)$$

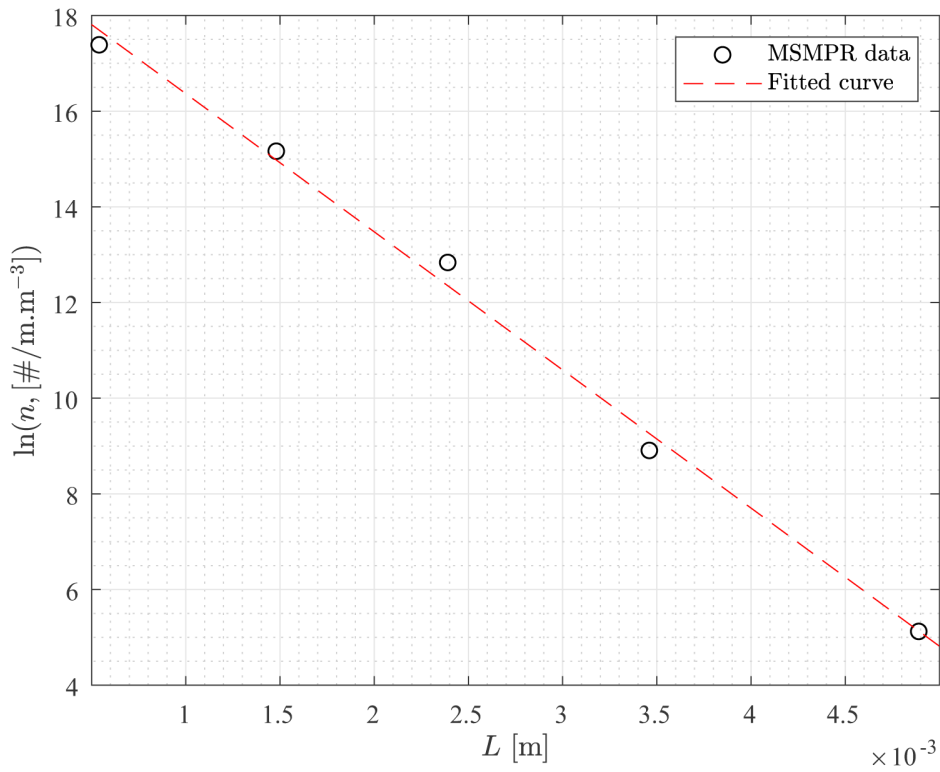


Figure 1: Size distribution of KNO₃ crystals from a MSMPR experiment.

The values computed from the above equations are tabulated below.

Parameters	Symbols	Units	Values
Crystal Growth Rate	G	m/s	2.1641e-08
Nucleation Rate	B	#.m ⁻³ s ⁻¹	4.9597
Mean Crystal Length	L_{mean}	mm	1.4

Table 2: Parameters obtained from MSMPR experiment

3 Design Decisions

A few design decisions have to be made for the crystallizer to start with. These decisions involve the choice of the crystallization method, the type of crystallizer and the operating parameters of the crystallizer. These design choices follow from the given operation parameters of the weight fraction (w_{feed}) and the feed flow rate ($\phi_{v,\text{feed}}$).

3.1 Determination of Feed Temperature

The feed temperature is obtained by linear interpolation of the temperature values from the solubility curve for a given percentage weight fraction of KNO_3 in the solution. The equilibrium concentration, C_{eq} , can be determined from equation 6.

$$C_{\text{eq}} = \frac{\dot{m}_{\text{KNO}_3}}{\dot{m}_{\text{prod}}} \quad (6)$$

The mass of KNO_3 can be obtained using the expression given below.

$$w_{\text{feed}} = \frac{\dot{m}_{\text{KNO}_3}}{\dot{m}_{\text{KNO}_3} + \dot{m}_{\text{water}}} \quad (7)$$

The saturation temperature that corresponds to the percentage weight fraction of KNO_3 at $C_{\text{eq}} = 0.35$ g/g of solution is considered as the feed temperature.

The solubility of KNO_3 (in wt%) in water is plotted from the given values of mass of KNO_3 in grams that can be dissolved in 100 grams of water for different temperatures as shown in the figure given below. Through linear interpolation from the following plot, the **feed temperature** is determined to be **34.73 °C**.

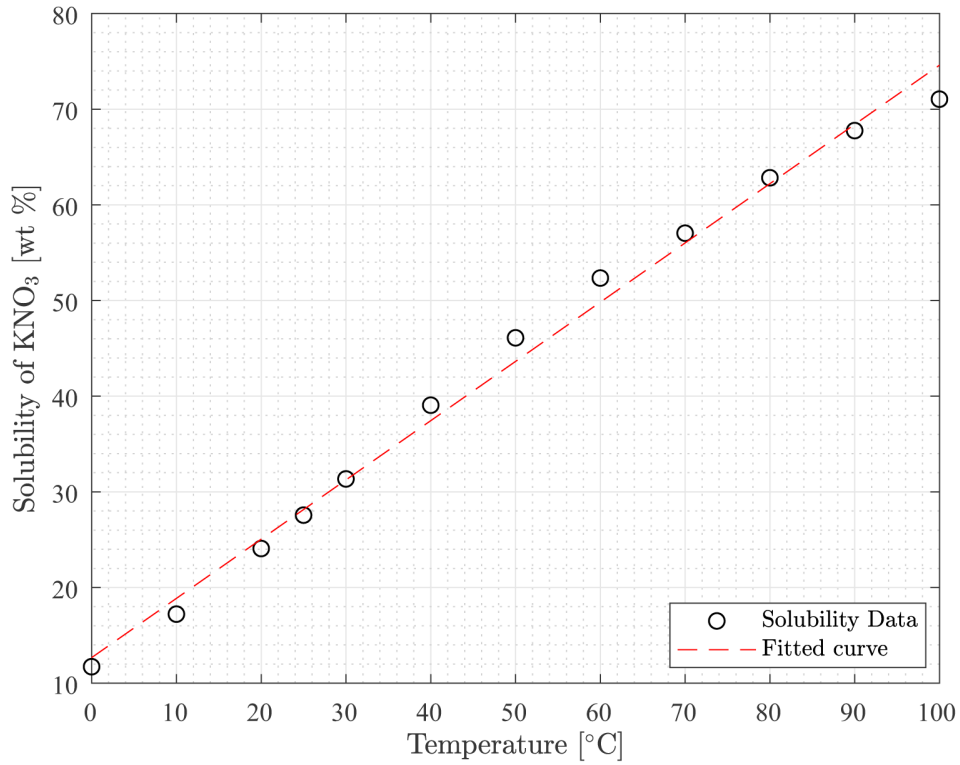


Figure 2: Variation of solubility of KNO_3 in water with change in temperature; for $C_{\text{eq}} = 35\%$, $T = 34.73^\circ\text{C}$.

3.2 Crystallization Method

The crystallization method can be selected from the figure given below. The slope of the solubility curve obtained using linear regression depicts the behavior of solubility with respect to change in temperature. For the obtained values of $C_{\text{eq}} = 0.35$ g/g of solution and $dC/dT = 0.0062$, **cooling crystallization** method is chosen to be appropriate.

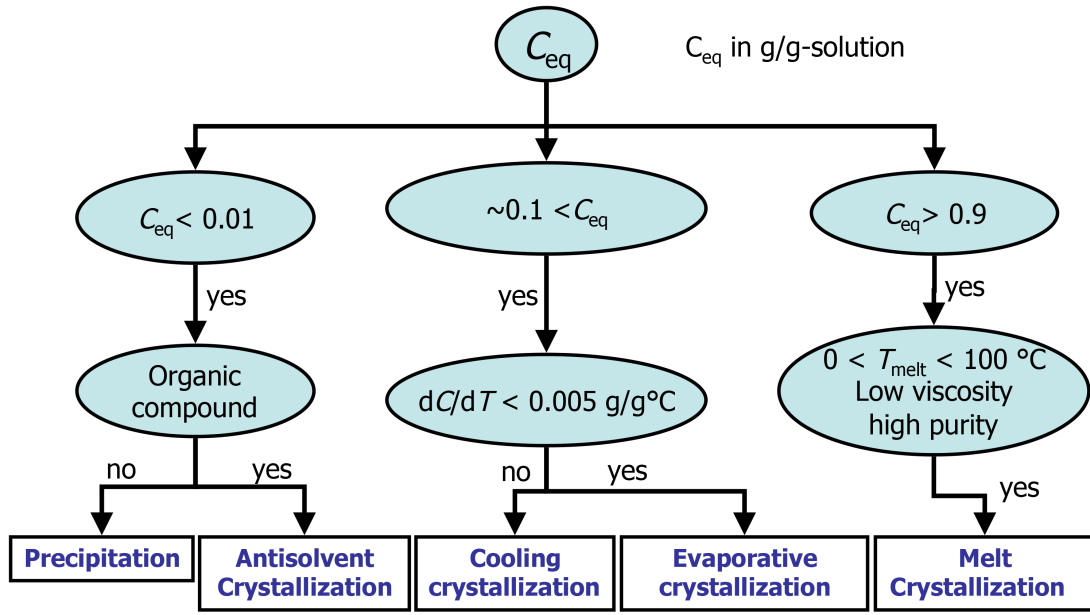


Figure 3: Selection of crystallization method from [2]; for $C_{eq} = 0.35$ g/g of solution & $dC/dT = 0.0062$, cooling crystallization is recommended.

A simple schematic of the cooling crystallization method is shown below.

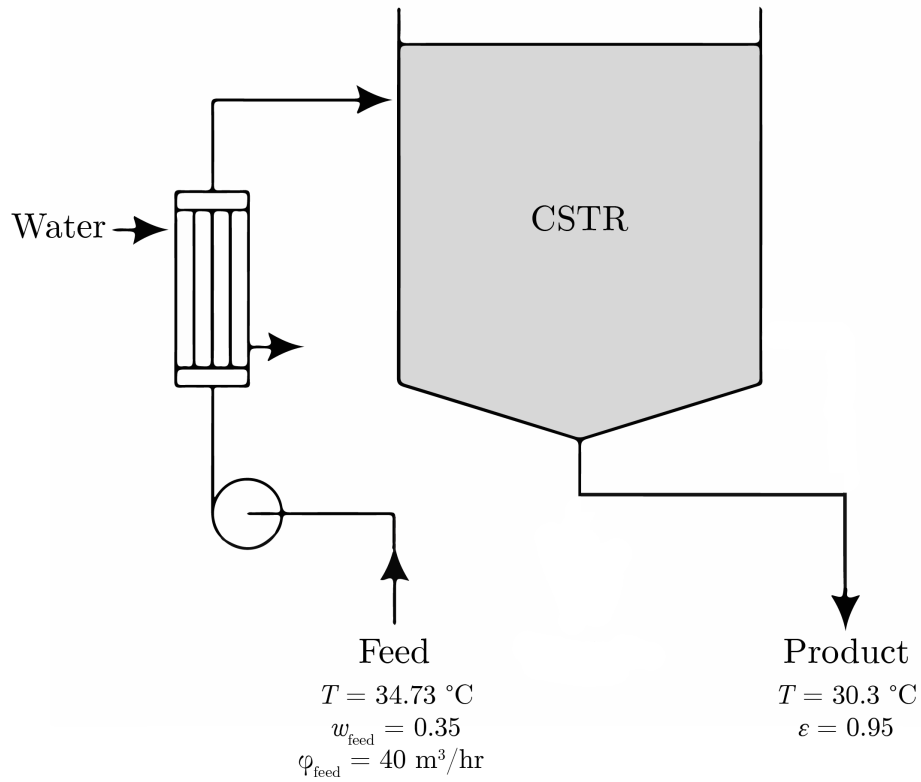


Figure 4: Schematic of cooling crystallization process

4 Mass Balance

4.1 Estimation of Product Composition

The crystallizer equipment consists of two streams, the feed stream entering and the product stream leaving. Although, it is possible to re-circulate a fraction of the product stream back into the feed stream, it not considered in this case as it does not concur with the industrial practice. The composition of the stream, volumetric flow rate of the product and the operating temperature can be determined accordingly from the mass balance of the streams entering and leaving the crystallizer.

The solid fraction (fraction of crystals in the product) can be defined as the mass production rate of crystal to the total mass of the product as per the below given relation.

$$\begin{aligned}\frac{\dot{m}_{\text{cr}}}{\dot{m}_{\text{prod}}} &= 1 - \epsilon \\ \frac{\rho_{\text{cr}} \phi_{\text{cr}}}{\rho_{\text{sol}} \phi_{\text{v,feed}}} &= 1 - \epsilon \\ \phi_{\text{cr}} &= (1 - \epsilon) \left(\frac{\rho_{\text{sol}}}{\rho_{\text{cr}}} \right) \phi_{\text{v,feed}}\end{aligned}\tag{8}$$

At the inlet of the crystallizer, it is given that $w_{\text{feed}} = 0.35$. Hence, we can relate the mass flow rate of KNO_3 at the inlet to the total feed flow rate from the expression given below.

$$\begin{aligned}\rho_{\text{sol}} \phi_{\text{KNO}_3,\text{in}} &= w_{\text{feed}} \rho_{\text{sol}} \phi_{\text{v,feed}} \\ \phi_{\text{KNO}_3,\text{in}} &= w_{\text{feed}} \phi_{\text{v,feed}}\end{aligned}\tag{9}$$

Using component balance of KNO_3 , we get the following relation.

$$\begin{aligned}\rho_{\text{sol}} \phi_{\text{KNO}_3,\text{in}} &= \rho_{\text{sol}} \phi_{\text{KNO}_3,\text{out}} + \rho_{\text{cr}} \phi_{\text{cr}} \\ \phi_{\text{KNO}_3,\text{out}} &= \phi_{\text{KNO}_3,\text{in}} - \left(\frac{\rho_{\text{cr}}}{\rho_{\text{sol}}} \right) \phi_{\text{cr}}\end{aligned}\tag{10}$$

From total mass balance between inlet and outlet streams, we get the following relation.

$$\begin{aligned}\rho_{\text{sol}} \phi_{\text{v,feed}} &= \rho_{\text{sol}} \phi_{\text{v,sol}} + \rho_{\text{cr}} \phi_{\text{cr}} \\ \phi_{\text{v,sol}} &= \phi_{\text{v,feed}} - \left(\frac{\rho_{\text{cr}}}{\rho_{\text{sol}}} \right) \phi_{\text{cr}}\end{aligned}\tag{11}$$

The weight fraction of KNO_3 in the liquid product stream can be determined from the equation given below.

$$w_{\text{prod}} = \frac{\phi_{\text{KNO}_3,\text{out}}}{\phi_{\text{v,sol}}}\tag{12}$$

The values of the respective parameters obtained from the equations 8, 9, 10, 11 and 12 are tabulated below.

Parameters	Symbols	Units	Values
Crystal Production Rate	ϕ_{cr}	m^3/hr	1.19
Flow Rate of KNO_3 at Inlet	$\phi_{\text{KNO}_3,\text{in}}$	m^3/hr	14
Flow Rate of KNO_3 at Outlet	$\phi_{\text{KNO}_3,\text{out}}$	m^3/hr	12
Flow Rate of Liquid Product	$\phi_{\text{v,sol}}$	m^3/hr	38
Weight Fraction of Liquid Product	w_{prod}	-	0.3158

Table 3: Parameters obtained from mass balance

Note that the density of the product stream was considered to be same as the density of feed stream for the above mass balance calculations. This can be justified by the fact that the variation between the feed temperature and the obtained operating temperature is very less and hence, the variation in density can be considered to be very minimal. Although, in reality, there is a small density variation that might cause a small error in the mass balance done by this approach.

4.2 Estimation of Operating Temperature

The operating temperature of the crystallizer can be obtained by linear interpolation of the solubility curve for the obtained weight fraction of the liquid product. Hence, the **operating temperature** is found to be **30.295 °C**. The obtained operating temperature is less than the feed temperature as expected for a cooling crystallization process.

4.3 Estimation of Product Flow Rate

The volumetric flow rate of the product can be obtained from the equation given below. Here, the value of w_{cr} is assumed to be 1 as the crystals are not hydrated and the liquid fraction of the feed, ϵ_{feed} is also assumed to be 1 as the entering feed stream contains saturated liquid only.

$$\phi_{v,prod} = \frac{\epsilon_{feed} \phi_{v,feed} \rho_{sol}}{\epsilon \rho_{sol} + (1 - \epsilon) \rho_{sol}} \quad (13)$$

The volumetric flow rate of the product is calculated to be 0.0107 m³/s or 38.6847 m³/hr.

4.4 Estimation of Production Rate of Crystals

The mass production rate of crystals is determined using the relation given below.

$$\dot{m}_{cr} = \phi_{cr} \rho_{cr} \quad (14)$$

The mass production rate of crystals is determined to be 0.6944 kg/s or 60 ton/day. Hence, **continuous operation mode** for the crystallizer is chosen as recommended for production rates higher than 50 tons/day.

5 Energy Balance

The cooling crystallizers are generally operated with jacket instead of an external heat exchanger as shown in figure 5. So, the heat energy transferred by the feed stream to the fluid inside the jacket (typically, water) can be obtained using an energy balance between the feed stream and the water in the jacket. The heat energy required can be computed as shown below.

$$Q = \dot{m}_{feed} C_{p,liquid} T_{feed} - (\dot{m}_{sol} C_{p,liquid} T_{oper} + \dot{m}_{cr} C_{p,cr} T_{oper}) \quad (15)$$

The mass flow rates of feed stream and liquid product stream are calculated to be 13.8889 kg/s and 13.1944 kg/s respectively. Hence, the **total heat energy** is found to be **0.7797 MW**.

The coolant (water) inside the jacket is considered to be at ambient temperature of 20°C initially and its mass flow rate is assumed to be 20 kg/s. The heat lost by feed stream is transferred to the water inside jacket and hence the outlet temperature of water will rise. This can be determined using the energy balance given below.

$$Q = \dot{m}_w C_{p,w} (T_{out,w} - T_{in,w}) \quad (16)$$

The outlet temperature of water is obtained from the above equation as 29.32 °C.

The total area of heat exchange can be determined using equation 17. The overall heat transfer coefficient is given as 800 W/m²K. Assuming counter-current flow, the logarithmic mean temperature difference (ΔT_{lm}) can be determined using the inlet and outlet temperatures of the feed stream and water respectively and is found as 7.5972 °C.

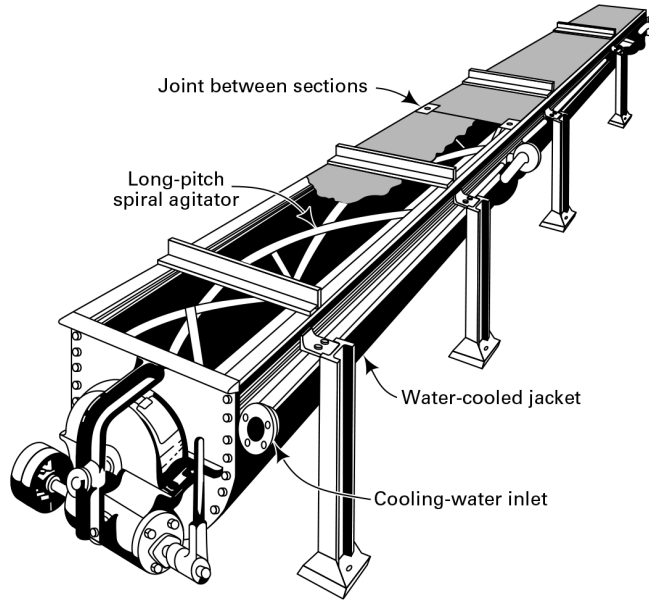


Figure 5: Swenson-Walker continuous cooling crystallizer

$$A = \frac{Q}{U \Delta T_{lm}} \quad (17)$$

The required **total area** of heat exchange equals **128.28 m²**. The **total heat capacity** required for the process as per equation 18 is found to be **1122.7 kJ/kg** of crystal.

$$Q_{cr} = \frac{Q}{\dot{m}_{cr}} \quad (18)$$

6 Final Design Parameters and Process Flow Sheet

The volume of the crystallizer can be determined assuming the same residence time as in the MSMPR experiment using the equation given below.

$$V = \phi_{v,prod} \tau \quad (19)$$

The **volume of the crystallizer** is estimated at **171.93 m³**.

The chemical composition and operating parameters obtained for each stream is tabulated below.

Parameters	Streams					
	Feed			Product		
	Symbols	Units	Values	Symbols	Units	Values
Volumetric Flow Rate	$\phi_{v,feed}$	m ³ /hr	40	$\phi_{v,prod}$	m ³ /hr	38.6847
Composition	w_{feed}	-	0.35	w_{prod}	-	0.3158
Liquid Fraction	ϵ_{feed}	-	1	ϵ_{prod}	-	0.95
Temperature	T_{feed}	°C	34.73	T_{oper}	°C	30.3

Table 4: Final design and operating parameters

The process flow diagram that specifies the properties, composition and operating conditions of each stream involved is depicted in figure 6.

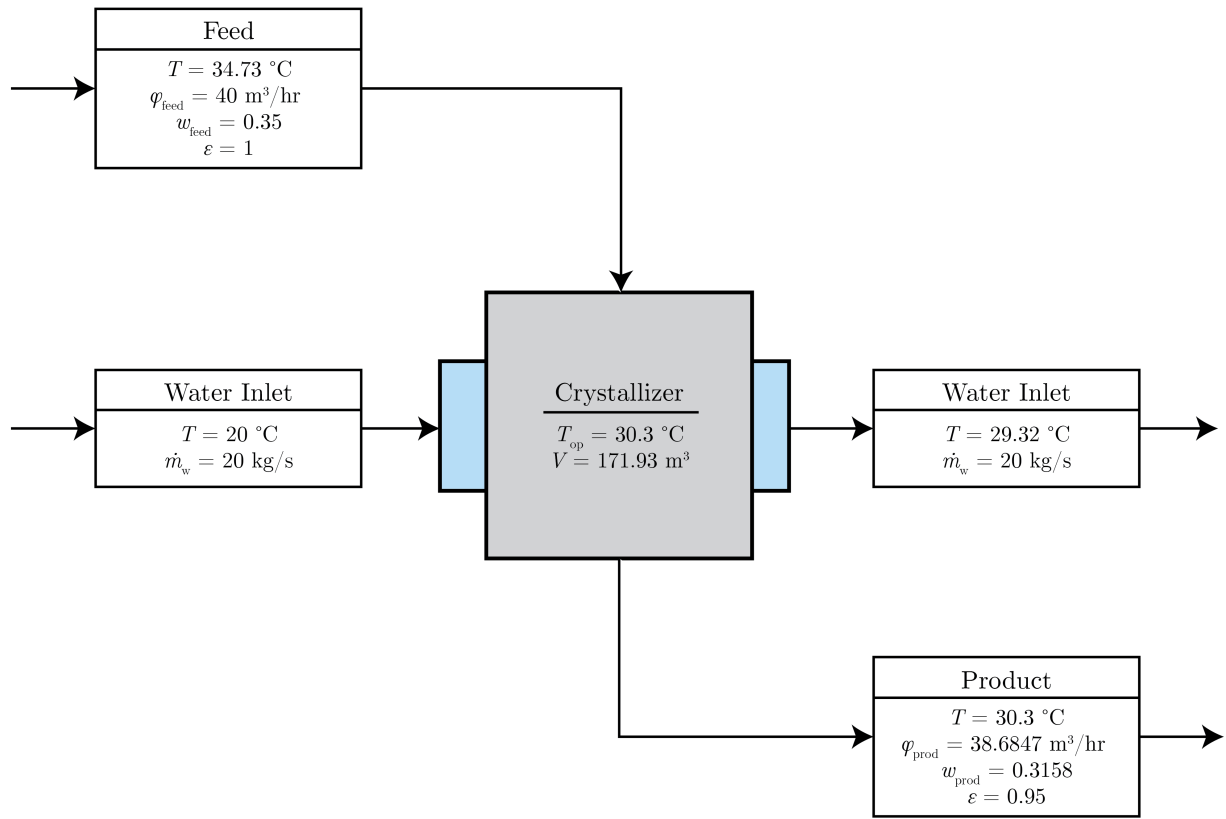


Figure 6: Process flow sheet

The design process can be further continued as a rigorous design of the crystallizer and a jacket which acts as a heat exchanger, cooling the feed stream. However, the specific design of the crystallizer is out of scope of this assignment.

Problem 2

Crystallization of Sodium and Potassium Chloride from Saline Wastewater Stream

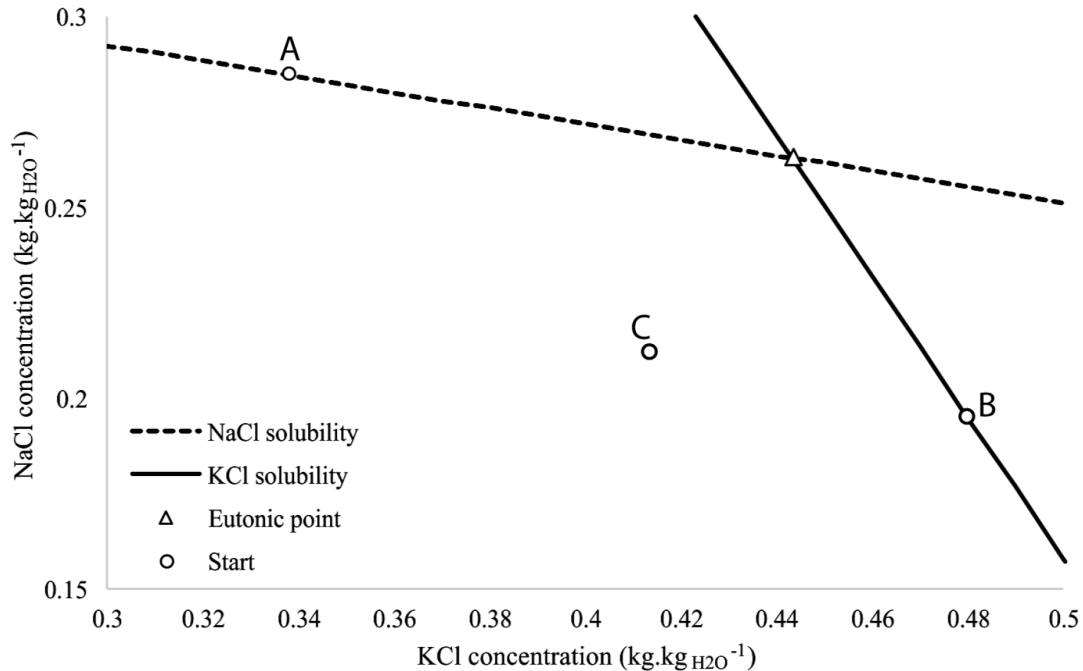


Figure 7: Solubility curves of NaCl and KCl

(a) How does the composition of the salts change due to evaporation?

Solution. Initially, at point A, NaCl in the solution is saturated as the point lies on the solubility curve of NaCl whereas the KCl in the solution is under-saturated as the point lies below the solubility curve of KCl at the given temperature of 110 °C. When evaporation occurs, NaCl starts to crystallize while KCl remains dissolved. When water is removed by evaporation, the concentration of KCl increases and that of NaCl decreases along the NaCl solubility curve. Interpreting the same with respect to figure 7, the system moves from A towards the eutonic point.

Similarly, at point B, KCl in the solution is saturated whereas the NaCl in the solution is under-saturated. When evaporation occurs, KCl starts to crystallize while NaCl remains dissolved. When water is removed due to evaporation, the concentration of NaCl increases and that of KCl decreases along the KCl solubility curve. In figure 7, this may be interpreted as the system moving from point B towards the eutonic point.

At point C, both NaCl and KCl in the solution are under-saturated and hence, crystallization does not occur on evaporation until either or both of the concentrations cross their respective solubility curves to become super-saturated. Hence, when evaporation occurs, both NaCl and KCl remain dissolved. This can be interpreted in figure 7 as the system moving from point C towards any one of the solubility lines after which the above two scenarios might occur.

(b) What happens to the composition and to the crystals when the solution reaches the eutonic concentration?

Solution. When the solution reaches the eutonic concentration (concentration at the eutonic point), both NaCl and KCl are crystallized simultaneously without any change in the composition of the solution. The crystallization of both the components of the solution will have the same crystallization rates.

(c) Is it possible to recover pure salt streams?

Solution. It is possible to recover just one component, either NaCl or KCl, from the stream, given the initial composition, until the system reaches its eutonic point. This follows the fact that crystallization of one component from supersaturation pushes the system to its eutonic point. Therefore, a single component can be extracted from the solution until the solution reaches the eutonic point.

Once the solution reaches the eutonic point, it is not possible to recover pure salt streams as both the components have similar crystallization rates and crystallize simultaneously. Hence, the process of evaporation must be controlled and monitored so as to prevent the concentrations from becoming eutonic in order to obtain pure salt streams. However, there is no possibility of a component in the solution to be recovered completely as a pure substance through this method.

(d) Can you propose a different method for this process? Say which one and cite advantages of the new process and disadvantages of the evaporative one.

Solution. One of the different methods to carry out this process apart from evaporation is through Eutectic Freeze Crystallization (EFC). By EFC, pure form of water and salt can be obtained and further separated using the difference in density of the crystals. It is less energy-intensive and operates at relatively lower temperatures when compared to the evaporative method which requires high temperature, consumes high energy and also requires more complicated equipment.

References

- [1] J.D. Seader, Ernest J. Henley, and D. Keith Roper. *Separation Process and Principles, 3rd Edition*. John Wiley & Sons, Inc., 2011.
- [2] Equipment for Heat and Mass Transfer - Crystallisation 3,
<https://brightspace.tudelft.nl/d21/1e/content/194619/viewContent/1400926/View>
- [3] Frederico M. Penha, Gustavo P. Zago, Yuri N. Nariyoshi, André Bernardo, and Marcelo M. Seckler *Simultaneous Crystallization of NaCl and KCl from Aqueous Solution: Elementary Phenomena and Product Characterization*. Crystal Growth & Design 2018 18 (3), 1645-1656.