

# Assignment 1 Mass transfer

Crystallization

## Group 29

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# **1 Introduction**

This is the first assignment in the mass transfer part of the course Equipment for heat and mass transfer. We will answer a number of questions related to the process of crystallization.

## 2 Question 1

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is to be produced in a Swenson-Walker crystallizer by cooling to 290 K a solution of anhydrous  $\text{Na}_2\text{SO}_4$  which saturates between 300K and 290 K. If cooling water enters and leaves the unit at 280 K and 290 K respectively and evaporation is negligible, how many sections of crystallizer, each 5 m long will be required to process 0.5 kg/s of the product? The solubilities of anhydrous  $\text{Na}_2\text{SO}_4$  in water are 40 and 14 kg/100 kg water at 300 K and 290 K respectively, the mean heat capacity of the liquor is 3.8 KJ/kg K and the heat of crystallization is 230 KJ/kg. For the crystallizer, the available heat transfer area is 7 m<sup>2</sup>/m length, the overall coefficient of heat transfer is 0.3 kW/m<sup>2</sup> K and the molecular masses are  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 322$  kg/kmol and  $\text{Na}_2\text{SO}_4 = 142$  kg/kmol.

### 2.1 Solution

It is given that a crystallizer section is 5 m long and that the available heat transfer area is 7 m<sup>2</sup>/m. This means that the heat transfer area of one section,  $A = 35$  m<sup>2</sup>.

Applying mass balance for 100 kg of water in inlet and outlet,

Mass balance for water:

$$\text{Inlet water (100 kg)} = (x) \text{ kg in crystal} + (100 - x) \text{ kg in outlet solution}$$

Mass balance for  $\text{Na}_2\text{SO}_4$ :

$$\text{Inlet Na}_2\text{SO}_4 \text{ (40 kg)} = x \left( \frac{322}{18 \times 10} \right) \text{ kg in crystal} + (100 - x) \frac{14}{100} \text{ kg in solution}$$

Solving for  $x$ , we find  $x=40.06$  kg for 100 kg of inlet water. The total crystal mass is found to be 71.68 kg for 100 kg of water. which is 140 kg of inlet solution. Now for 0.5 kg/s of crystal production, 0.9765 kg/s of inlet solution is needed.

The heat required can be found with the following formula:

$$Q = \dot{m}_{\text{crystal}} \Delta H_{\text{crystallization}} + \dot{m}_{\text{inlet\_solution}} c_p \Delta T = 152.1 \text{ kW} \quad (1)$$

Now, the heat transfer area required  $A_r$  with given overall heat transfer coefficient  $U$  is given by,

$$A_r = \frac{Q}{U \Delta T_{lm}} = 50.7 \text{ m}^2 \quad (2)$$

where  $\Delta T_{lm}$  (= 10K) is the logarithmic mean temperature difference for counter current flow. The number of crystallizers required is found to be,

$$\frac{A}{A_r} \approx 2 \text{ crystallizers}$$

### 3 Question 2

An MSMPR-type crystallizer is to be designed to produce 1,000 kg/h of crystals of the heptahydrate of magnesium sulfate with a predominant crystal size of 500  $\mu\text{m}$ . The magma will be 15 %vol crystals. The temperature in the crystallizer will be 50 °C and the residence time 2 h. The densities of the crystals and mother liquor are 1680 and 1320 kg/m<sup>3</sup>, respectively. Determine: (a) the exiting flow rates in m<sup>3</sup>/h of crystals, mother liquor, and magma (b) the crystallizer volume in litres, if the vapour space equals the magma space (c) the approximate dimensions in feet of the crystallizer, if the body is cylindrical with a height equal to twice the diameter (d) the required crystal growth rate in m/h (e) the necessary nucleation rate in nuclei/h-m<sup>3</sup> of mother liquor in the crystallizer (f) the number of crystals produced per hour.

#### 3.1 Solution

(a) The first step will be to determine the volume flow rates.

$$\dot{V}_{\text{crystal}} = \frac{\dot{m}_{\text{crystal}}}{\rho_{\text{crystal}}} = 0.595 \text{ m}^3/\text{hr} \quad (3)$$

$$\dot{V}_{\text{magma}} = \frac{\dot{V}_{\text{crystal}}}{\% \text{vol crystals}} = 3.968 \text{ m}^3/\text{hr} \quad (4)$$

$$\dot{V}_{\text{liquor}} = \dot{V}_{\text{magma}} - \dot{V}_{\text{crystal}} = 3.373 \text{ m}^3/\text{hr} \quad (5)$$

(b) Now the exiting flow rates are known the crystallizer volume in litres can be computed. This can be achieved by multiplying the magma volume rate with the residence time. Then the volume of the magma is found. The volume of the magma is assumed to be equal to the vapour volume, which means that the volume of the crystallizer can be found by multiplying the magma volume with two.

$$V_{\text{crystallizer}} = 2\dot{V}_{\text{magma}}t_{\text{residence}} = 15.873 \text{ m}^3 \quad (6)$$

(c) The crystallizer is cylindrical with a diameter half the height.

$$d = \left( \frac{2V_{\text{crystallizer}}}{\pi} \right)^{\frac{1}{3}} = 2.16 \text{ m (or) } 7.094 \text{ ft} \quad (7)$$

Now the diameter of the crystallizer is known the height can easily be found by multiplying the diameter with two.

$$H = 4.32 \text{ m (or) } 14.188 \text{ ft}$$

(d) The required crystal growth rate can be found with the following formula

$$G = \frac{d}{3t_{\text{residence}}} = 80.33 \text{ } \mu\text{m} \quad (8)$$

(e) The nucleation rate is determined by the following relation

$$B = \frac{9\dot{m}_{\text{crystal}}}{2f_v\rho_{\text{crystal}}V_{\text{liquor}}t_{\text{residence}}d^3} = 6.35 \times 10^9 \text{ nuclei}/(m^3 \text{ h}) \quad (9)$$

The factor  $f_v$  is the volumetric shape factor and taken to be equal to 0.5.

(f) Finally the crystal production rate is given by

$$\text{Crystal production rate} = BV_{\text{liquor}}t_{\text{residence}} = 4.28 \times 10^{10} \text{ crystals/h} \quad (10)$$

## 4 Question 3

Using the following data, compare the effect of supersaturation ratio between 1.02 to 1.03 on the primary homogeneous nucleation of  $\text{AgNO}_3$ ,  $\text{NaNO}_3$ , and  $\text{KNO}_3$  from aqueous solutions at  $25^\circ\text{C}$ . Crystal density of  $\text{AgNO}_3 = 4350 \text{ kg/m}^3$  and Interfacial tension  $= 0.0025 \text{ J/m}^2$ . Crystal density of  $\text{NaNO}_3 = 2260 \text{ kg/m}^3$  and Interfacial tension  $= 0.0015 \text{ J/m}^2$ . Crystal density of  $\text{KNO}_3 = 2110 \text{ kg/m}^3$  and Interfacial tension  $= 0.0030 \text{ J/m}^2$ .

### 4.1 Solution

We've taken on this question by ranging the supersaturation ratio from 1.02 to 1.03 in 15 equidistant points.

The nucleation rate is calculated as follows,

$$B = A \exp \left( \frac{-16\pi V_m \sigma^3}{3\nu^2 (RT)^3 \ln^2(S)} \right) \quad (11)$$

where A is assumed to be  $10^{30}$  for homogeneous nucleation,  $N_a$  is avagadro number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ),  $\sigma$  is the interfacial tension, S is the super saturation ratio,  $V_m$  is the molar volume, R is the universal gas constant ( $8.3145 \text{ J/(mol.K)}$ ) and  $\nu$  is the number of ions which is 2 for all 3 materials. Molar volume is calculated as,  $V_m = \frac{\text{Molar mass}}{\rho}$

	Molar mass [g/mol]
$\text{AgNO}_3$	169.6
$\text{NaNO}_3$	85
$\text{KNO}_3$	101.1

Table 1: Molar mass of substances in the crystallizer.

First the nucleation rate was compared over the supersaturation ratio range. It should be noted that a higher saturation ratio leads to a higher nucleation rate.

Next the effect of the saturation ratio on the chrystal size is evaluated. The interfacial tension of the substances in the crystallizer has been denoted below.

	Interfacial tension [mN/m]
$\text{AgNO}_3$	0.0025
$\text{NaNO}_3$	0.0015
$\text{KNO}_3$	0.0030

Table 2: Interfacial tension of substances in the crystallizer.

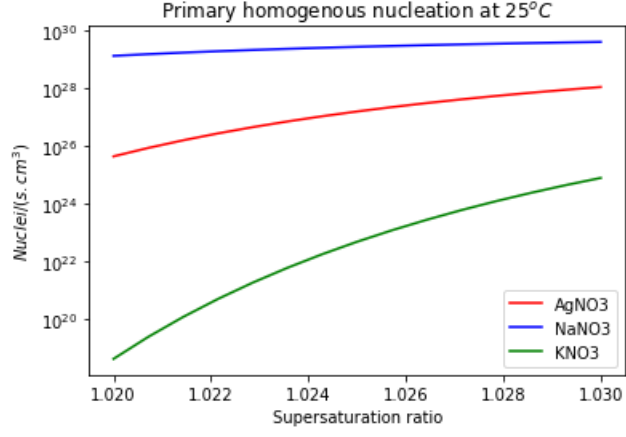


Figure 1: Nucleation rate vs. supersaturation ratio

The crystal diameter is calculated with the following formula.

$$D = \frac{4i_t V_m}{nRT \ln(S)} \quad (12)$$

In this formula  $i_t$  is the interfacial tension. The molar volume of the crystal is represented by  $V_m$ . The number of ions per molecule is given by  $n$  and is equal to 2,  $T$  is the temperature at which crystallization is taking place which is 298.15 K.  $R$  is the universal gas constant and  $S$  is the supersaturation ratio.

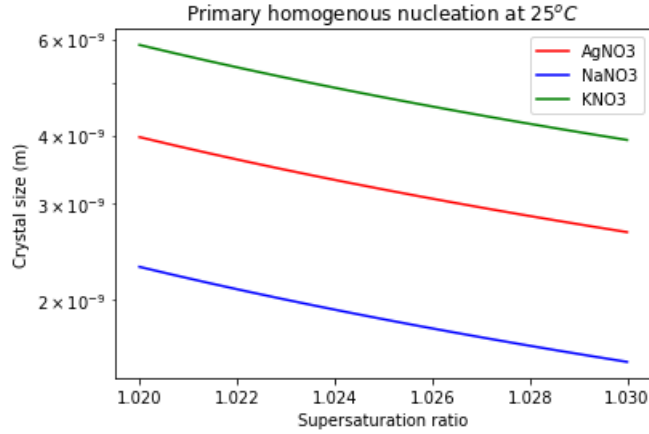


Figure 2: crystal size vs. supersaturation ratio

As the saturation ratio increases the crystal size decreases.