STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LI, 1, 2006

# STUDIES ON THE NATRIUM SULPHATE SALTING-OUT CRYSTALLIZATION II. CRYSTALLIZATION KINETICS

**ADINA GHIRISAN, SIMION DRĂGAN, ALEXANDRU POP AND VASILE MICLĂUŞ***

**ABSTRACT.** The kinetic of nucleation and growing of the crystal nuclei in the salting-out crystallization of natrium sulphate were studied. The influence of kinetic parameters (energy consumption or *agitator power input*, temperature and growth rate) on the second nucleation was determined. The influence of the hydrodynamic conditions and of the temperature on the average size of the obtained crystals was discussed. A value of activation energy of $5.4 \bullet 10^4$ J/mol for the nucleation process was determined.

## Introduction

A crystallization operation consists of three basic steps: supersaturation (or supercooling), formation of crystal nuclei, and the subsequent growth of these nuclei into crystals [1]. Supersaturation may be achieved by cooling, evaporation of the solvent, addition of a precipitating agent, as a result of a chemical reaction, etc.

The conventional process of natrium sulphate crystallization through evaporation has many disadvantages: the high-energy requirement, the complexity of the installation with many steps and the complex process of separation of the obtained Glauber salt [2].

By the salting-out crystallization, by adding organic alcohol (methanol or ethanol) the solubility of the solute in the solvent supersaturated solution was reduced [3]. The equilibrium study of the salting-out crystallization has shown several advantages [3]:

a). The process can be operated at low temperature without output or input of energy in the crystallizer;

b). The construction of the installation is simple with lower cost of equipment and

c). Very pure crystals can be obtained because of high retention for the impurities of the mixed-solvent mother liquor.

To have a complete information about the process evolution in the case of salting-out crystallization of natrium sulphate the equilibrium data obtained in the first part of our study [3] are not enough. It is necessary to know more about the factors that can influence the nucleation and the crystal

* Faculty of Chemistry and Chemical Engineering "Babeş-Bolyai" University, 400028 Cluj-Napoca, Romania

growth kinetics: intensity of mixing between organic and inorganic phases, concentration of the sulphate in aqueous solution, crystal size evolution, etc.

**Nucleation**

The generation of ultramicroscopic particles in the process of nucleation is the sum of contributions by primary and secondary nucleation. Primary nucleation occurs in the absence of crystals, while secondary nucleation is attributed to the influence of existing crystals.
The rate of primary nucleation has been modelled by the power law expression [4]:

$$B = \frac{dN}{dt} = k_n (C - C^*)^n \quad (1)$$

where *B* is the number of nuclei formed per unit volume per unit time, *N* – the number of new nuclei per unit volume, $k_n$ – the rate constant, *C* – the instantaneous solute concentration, and *C** the solute concentration at saturation. The *(C-C*)* term is the driving force of the crystallization process, called the *supersaturation*. The exponent n is typically in the range of 3 to 4 [5].
When a supersaturated solution is in contact with particles of the crystallizing compound, secondary nucleation occurs. Experimental data from industrial crystallizers have indicated that secondary nucleation usually predominates. There are two types of secondary nucleation: shear nucleation and contact nucleation [3]. *Shear nucleation* occurs as a result of fluid shear on growing crystal faces, and *contact nucleation* happens because of crystal collision with each other and with the impeller and other vessel internal surfaces. The most widely used relation for the rate of secondary nucleation in crystallization is the following [6]:

$$B = \frac{dN}{dt} = k_B \cdot \rho_L{}^l \cdot (C - C^*)^b \quad (2)$$

where $k_B$ is the rate constant and $\rho_L$ is the suspension density. The exponent "*l* " ranges up 1.5, with 1 being the more probable value, the exponent *b* can be range up to 5 but has a most probable value of 2 [5].

**Crystal growth**

Crystal growth is the post nucleation process in which molecules are deposited on the surface of existing crystals. If crystal size is characterized by a characteristic dimension, *L*, it is convenient to express its linear growth rate by the equation [4]:

$$G \equiv \frac{dL}{dt} = k_g (C - C^*)^g \quad (3)$$

where $L$ is a characteristic dimension of the crystal and $k_g$ is an overall mass transfer coefficient; $k_g$ is in general depended on the crystal size, hydrodynamic conditions, temperature, the nature of the ions and the presence of impurities.

Crystal growth is actually a process that consists of two steps in series. In the fist step the solute molecules or ions must reach the crystal surface by means of diffusion. In the second one, at the surface, the solute must be integrated into the crystal lattice. These two processes may be described as:

Diffusion: $$G = k_d (C - C_i)^d \quad (4)$$

Surface integration: $$G = k_r (C_i - C^*)^r \quad (5)$$

where $C_i$ is the concentration at the interface between the liquid and the solid phase, $k_d$ and $k_r$ are the mass transfer coefficients. If surface integration is very fast compared with bulk diffusion, $k_r >> k_d$ and $k_g \approx k_d$.

In conclusion, the formation of a stable crystal nucleus in a homogeneous or a heterogeneous system is not an easy process. Not only must the requisite number of molecules agglomerate, but also they must become oriented into a fixed lattice.

In this research study we have tried to establish the crystal formation rate during salting-out crystallization of natrium sulphate considering the influence of different factors as density of suspension, power input as the specific consumption of energy for mass unit, and crystal growth rate and the efficiency of the separation process.

**Experimental**

The experimental research was carried out in a batch isothermal stirred vessel of 0.5 l, type MSMPR (Mixed Suspension, Mixed Product Removal), with a device for the measuring and controlling of the temperature. The used agitator is an impeller with diameter blade of 4 cm.

The growth rates were obtained through granulometric analysis. For the granulometric analysis the suspension samples collected in time were filtered, washed with alcohol, dried and then analysed by sieving. The nucleation rates were obtained from the induction time, defined as the time between realisation of the known supersaturation and the appearance of the visible crystal [7]. The numbers of the crystals were determined for a diluted sample using a Coulter-Counter device [7].

The intensity of the hydrodynamic conditions was evaluated by the energy consumption or power input.

The following parameters were investigated:

- the residence time in crystallizer 5 – 180 min,
- the consumption energy (agitator power input) 0.18 – 1.64 W/kg,
- the temperature 30 – 70 $^0$C.

**Results and Discussion**

**The Efficiency of Crystallization**

In this paper the efficiency of crystallization is defined as the ratio between the experimental obtained mass and the theoretical mass of the crystals. The data obtained from Fig. 1 have pointed out that the efficiency of the crystallization depends on the temperature and residence time in the crystallizer at constant energy consumption. The diagram from Fig. 1 shows that at a *specific energy consumption* of 0.18 W/kg a higher than 90 % efficiency can be obtained only by a residence time of 120 minutes and a temperature of 70 $^0$C. To explain this dependence we have performed some kinetic studies.

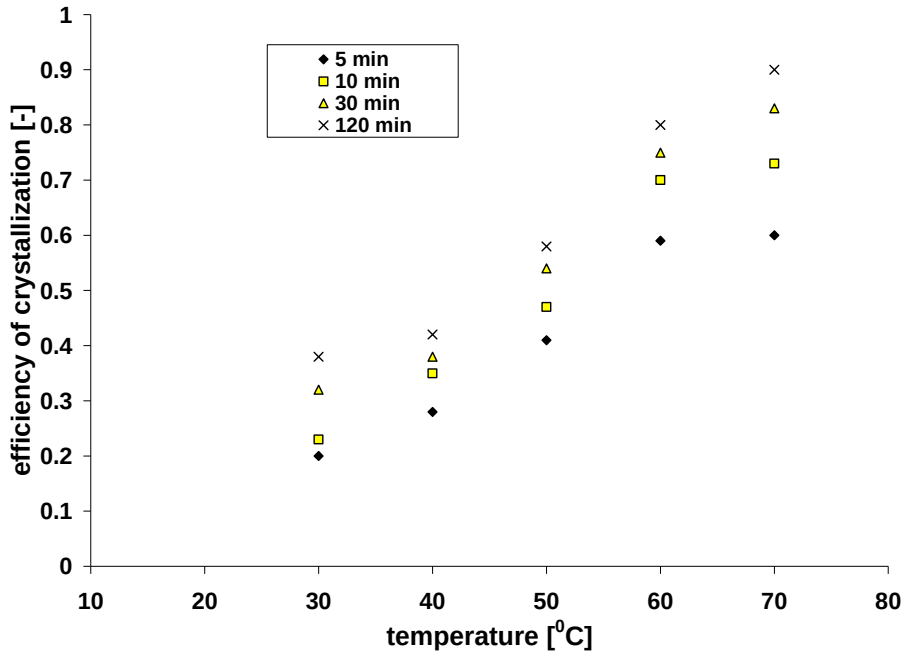


**Fig. 1.**
Efficiency of crystallization versus temperature at different residence timefor a power input of 0.18 W/kg.

**Crystallization Kinetics**

Estimates of nucleation and growth rates during crystallization can be obtained from the population balance analysis by batch experiments [4]. By making a mass balance on the number of crystals within a given size range between *L* and *L* +*ΔL*, the population balance equation for size independent growth in a perfectly mixed batch crystallizer with negligible breakage and agglomeration is:

$$\frac{\partial(\mathrm{nV})}{\partial \mathrm{t}} + \frac{\partial(\mathrm{nVG})}{\partial \mathrm{L}} = 0 \tag{6}$$

where *n* is the population density defined as the number of crystals of specific size per unit volume of crystallizer (number/$m^3m^1$), *L*- size of crystals at time t (m), *G* – overall linear growth rate of crystals (m/s).

The mass balance in the MSMPR crystallizer with ideal mixing can be obtained using the equation data (solubility curve) and definition of the moments of distribution as pointed by Randolph [8]. For an MSMPR crystallizer with ideal mixing, with constant volume, without agglomeration and breakage, which means that the growth rate independent of the size of the crystal is, operating at steady state, a solution of population balance (equation 6) is:

$$\mathrm{n} = \mathrm{n}_0 \exp\left(-\frac{\mathrm{L}}{\mathrm{G}\cdot\tau}\right) \tag{7}$$

When $\mathrm{L} \rightarrow 0$ the solution of equation (6) will be:

$$\mathrm{B}_0 = \mathrm{n}_0 \cdot \mathrm{G}_0 \tag{8}$$

The equation (8) suggests that the secondary nucleation rate $B_0$ (number/$m^3s^1$) is the product of population density $n_0$ (number of crystals/$m^4$) and the crystal growth rate $G_0$ (m/s), is defined as equation (3) has already shown.

There are many empirical expressions that correlate the second nucleation rate with the crystallization parameters. The mostly used for the contact nucleation is given by the next equation [9]:

$$\mathrm{B}_0 = \mathrm{k}_\mathrm{B} \cdot \rho_\mathrm{L}{}^{\mathrm{l}} \cdot \varepsilon^{\mathrm{r}} \cdot \mathrm{G}_0{}^{\mathrm{p}} \tag{9}$$

The analysis of equation (9) shows the dependence of the nucleation process on the suspension density ($\rho_L$) to a power exponent "*l*", on power input ($\varepsilon$) to a power exponent "*r*" and on growth rate ($G_0$) to a power exponent "*p*".

By operating on MSMPR crystallizer at steady state for different systems Mersmann [10] it has been concluded that the value of the exponent "*l*" = 1.

Because the effective nucleation rate $B_0$ is influenced by the crystal mass in crystallizer the density of the suspension will be replaced by the retention degree $\Phi$ defined by the equation:

$$\Phi = \frac{\rho}{\rho_S} \tag{10}$$

where $\rho$ is the suspension density and $\rho_S$ – the solid density.

So, the new equation of modified nucleation rate is:

$$\frac{B_0}{\Phi} = k_B \cdot \rho_S \cdot \varepsilon^r \cdot G_0{}^p \tag{11}$$

For the determination of the power exponents we have assumed that the equation (11) can be simplified to the form:

$$\frac{B_0}{\Phi} = K_1 \cdot G_0{}^p \tag{12}$$

A straight line on the double log scale can represent this equation for all used consumption energy (Figure 2). The slope of the straight line corresponds to the value of the power exponent "*p*". The average value is 1.045, which corresponds to the literature values (1 – 3) [11].

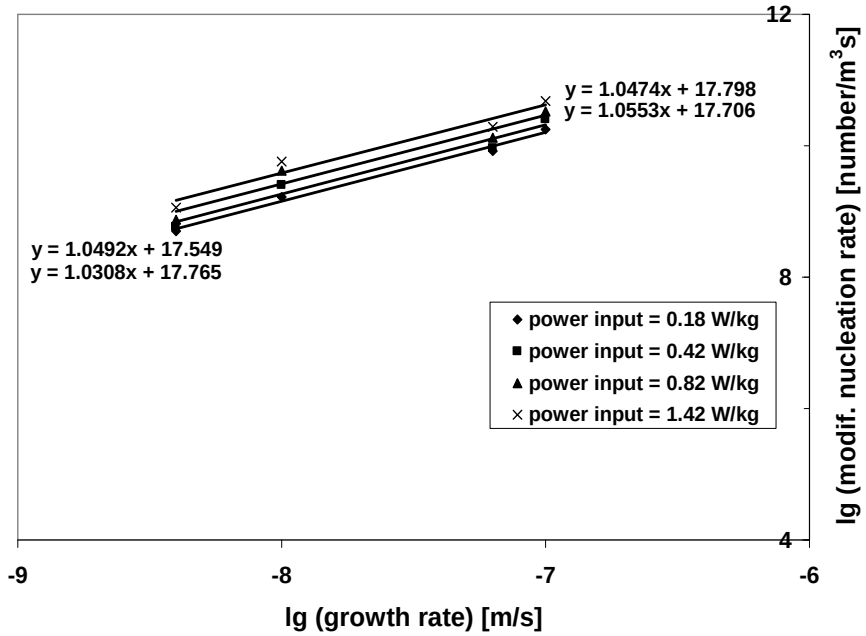


**Fig 2.**
Determination of the power exponent “p”.

In order to obtain the value of the power exponent “*r*” the equation (11) was simplified to the form:

$$\frac{B_0}{\Phi} = K_2 \cdot \varepsilon^r \tag{13}$$

From the slope of the curves log $B_0/\Phi$ versus log $\varepsilon$ an average value of r = 0.61 was obtained (Figure 3), which corresponds to the literature values (0.6 – 0.7) [11]. The results have shown the maintenance of a constant slope at different power input of stirrer.

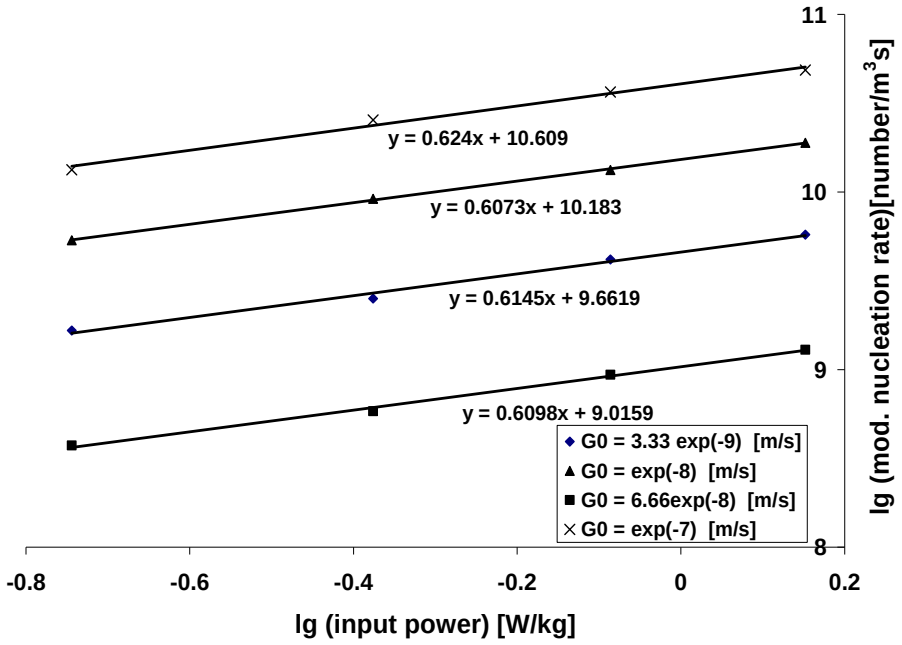


**Fig. 3.**
Determination of the power exponent “r”.

The influence of the temperature on the nucleation rate is represented by the constant rate for secondary nucleation $k_B$:

$$k_B = \frac{B_0}{\rho_S \cdot \Phi \cdot \varepsilon^{0.61} \cdot G_0^{1.045}} \tag{14}$$

as the equation of Arrhenius shows:

$$k_B = k_0 \cdot e^{-\frac{E_a}{RT}} \tag{15}$$

The plot log $k_B$ versus (1/T) leads to a straight line with a constant slope for different linear growth rates (Figure 4). From the slope of the straight line the activation energy $E_a = 5{,}4\ 10^4$ J/mol was obtained.

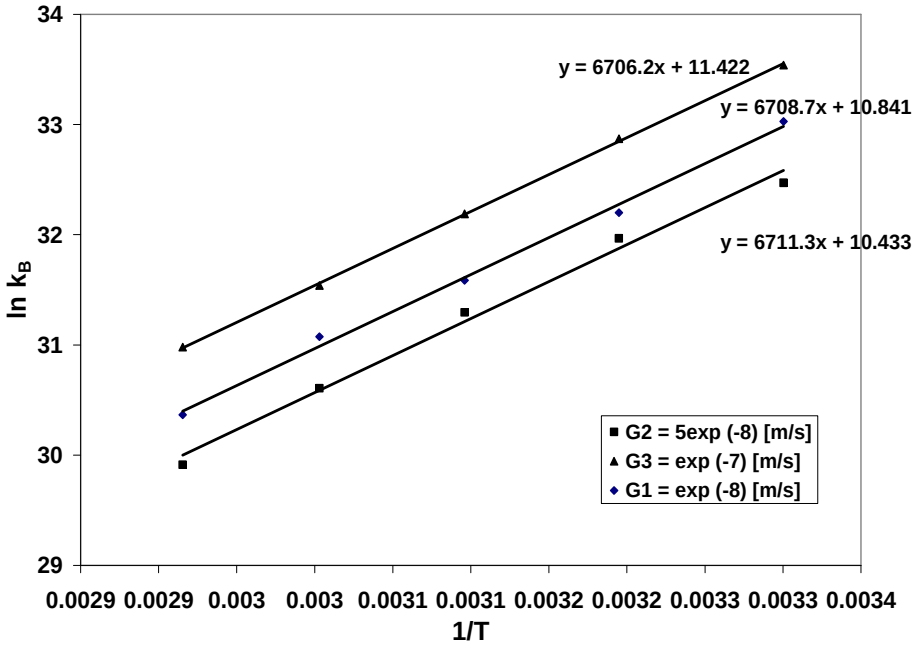


**Fig. 4.**
The influence of the temperature on the nucleation rate.

**Crystal size**

The granulometric analysis of the obtained natrium sulphate has shown that the average diameter of the crystals lies in the range 150 - 500 μm depending on the crystallization conditions. Sometimes the size of the crystal increases up to 1 mm, because of the agglomeration process that can be observed from the polycrystalline form of the particles visible only by microscopic analysis.

The analysis of the dependence of the average diameter of the crystals on the growth rate at a constant residence time can be calculated by the equation (16):

$$x_{50} = K \cdot G_0 \tag{16}$$

where $G_0$ is defined by the equation (3). The equation (3) has shown that the linear growth rate depends on hydrodynamic conditions and temperature by means of the $k_g$ coefficient.

In Figure 5 the experimental values of the average size of the crystals $x_{50}$ (mm) are plotted versus power input per unit mass ε (W/kg) at different temperatures. The linear dependence of the average diameter of the crystal on the power input at constant temperature was observed. At the same time the dependence of the crystal size on the temperature has shown that with the increase of the temperature, the average size of the crystals decreases for the same consumption of energy. The decrease of the average size of the particles simultaneously with the increase of the temperature can be explained through the decrease of the crystallization potential (C - C*), supersaturation having a higher influence on the growth rate than constant K.

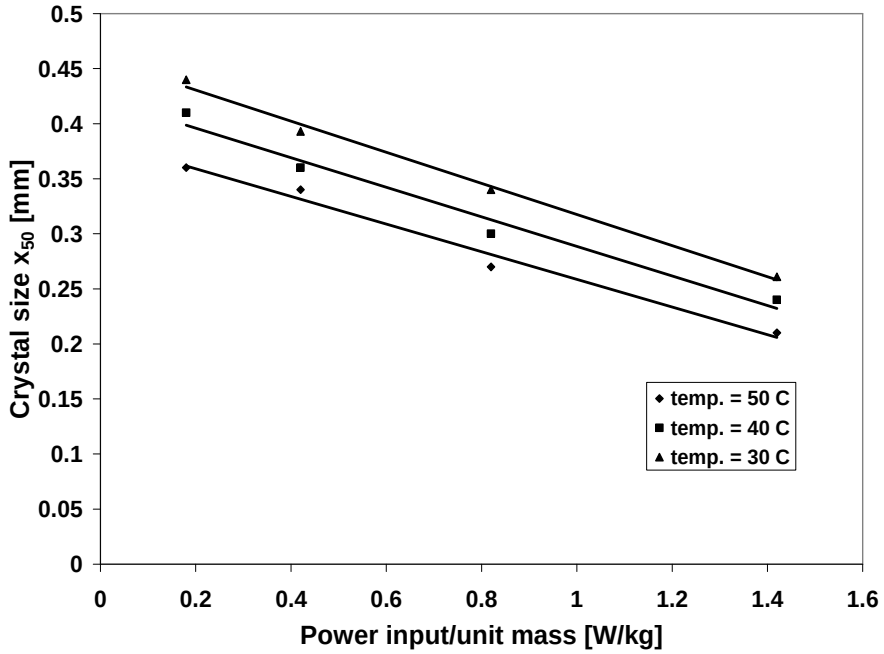


**Fig. 5.**
Crystal size versus specific consumption of energy.

**Conclusions**

The kinetic results have shown that the efficiency of the crystallization can be improved with the increase of the residence time and with the variation of the temperature in crystallizer.

By using the equation of population balance it was made possible to determine the specific influence of each parameter on the crystallization process.

The experimental measurements have shown that the second nucleation constant $k_B$ decreases with the increase of the temperature. From the Arrhenius equation the activation energy of nucleation $E_a$ = 5,4 $10^4$ J/mol was determined.

The dependence of the average diameter of the crystals on the power input $\varepsilon$ was also determined.

The obtained results have shown that the salting-out crystallization leads to superior sizes of the crystal comparing the classical evaporation process and to a rigorous control of the process.

## REFERENCES


1. Kirk-Othmer, "*Encyclopedia of Chemical Technology*", Second Edition, Ed. Wiley and Sons, Inc., **1965**
2. H. Poppe, *Chem. Proc. Eng*., **1968**, 12, 61 - 71
3. Al. Pop, A. Ghirişan, S. Drăgan and V. Miclăuş, *Studia Univ. Babeş-Bolyai, Chemia*, **2004**, 49(2), 195 - 201
4. N.S. Tavare, "*Industrial Crystallization*", Plenum Press, New York, **1995**
5. R.G. Harrison, P. Todd, Scott R. Rudge and D.P. Petrides, "*Bioseparations Science and Engineering*", N.Y. Oxford, Oxford Univ. Press, **2003**
6. W.J. Genck, "*Crystallization from solutions. In Handbook of Separations Techniques for Chemical Engineers*", 3nd, Ed. McGrow-Hill, New York, **1977**
7. L. Filipescu, M. Crețu, M. Mocioi and A. Zaharia, *Revista de Chimie*, **1981**, 32(4), 347 - 351
8. A. Randolph şi M. Larson, "*Theory of Particulate Process*", 2nd, Ed. Academic Press, San Diego, **1988**
9. J. Nyvlt, O. Sohnel, M. Matuchova and M. Broul, "*Kinetics of Industrial Crystallization*", Ed. Academic Praque, **1985**
10. A. Mersmann, *Chem. Ing.Tech*., **1982**, 54 (7), 631-643
11. M. Giulietti, M.M. Seckler, S. Derenzo, M. I. Re and E. Cekinski, *Braz. J. Chem. Eng*., **2001**, 18(4), 423 - 440