

EFFECT OF OFF-BOTTOM IMPELLER CLEARANCE ON NUCLEATION AND CRYSTAL GROWTH OF BORAX DECAHYDRATE IN BATCH COOLING CRYSTALLIZER

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Abstract. The main topic of this study was to estimate the impact of the off-bottom impeller clearance on the metastable zone width, nucleation kinetics and the crystal size distribution of borax decahydrate. The importance of impeller position was studied in baffled stirred crystallizer with a volume of about 2 L, equipped with straight four blade turbine (4-SBT) cooling at constant cooling rate. Metastable zone width was determined by visual method, while concentration changes during the process were monitored in line using ion-selective electrode. The nucleation behavior in the batch cooling crystallizer was presented according to Mersmann's criteria. On the basis of the experimental results and observations it is evident that in an agitated batch crystallizer metastable zone width, nucleation rate, crystal growth as well as crystal size distribution are significantly influenced by hydrodynamic regime in the system determined by impeller used and its position.

Key words: Crystallization; Borax; Mixing; Off-bottom clearance; Metastable zone width; Nucleation; Crystal growth; Crystal size distributions

1. INTRODUCTION

Borax decahydrate is a product of great industrial interest. It is the refined form of natural sodium borate used widely in detergent and cleaning formulations, as fungicide, disinfectant or herbicide. Borax has important role as an agent what modifies the structure of glasses, especially in the production of ultra thin screens. In order to produce crystals of borax with a specified purity and crystal size distribution (CSD) at minimum cost, it is necessary to operate the crystallizer at the optimum conditions.

Crystallization is usually carried out in a suspension and for this reason the study of crystallization requires knowledge of mixing. Mixing can have a dramatic effect on the properties of the product, including CSD, purity, morphology and polymorphic form. Regardless of size, each crystallizer requires a proper selection of the mixing characteristics. Choosing the proper position of the impeller in the crystallizer is one of imperatives for optimum mixing. Although it has been empirically known that the geometrical configuration in the crystallizer has a considerable effect on the product crystal size distribution, this problem has rarely been quantitatively investigated [1]. The aim of the present work is to investigate the effect of the off-bottom impeller clearance on the metastable zone width,

nucleation, crystal growth and product crystal size distribution and to clarify the mechanism involved.

2. EXPERIMENTAL PROCEDURE

2.1 Experimental set-up

The experimental work was carried out in a stirred batch cooling crystallizer with a volume of about 2 L. The solution was stirred by 4-SBT impeller, that is 4-straight blade turbine ($D/d_T = 0.4$; number of blades – 4; blade width – $0.12 D$). In all experiments the agitation speed was $N = 300$ rpm because at this speed the state of complete suspension was achieved. The crystallizer was the cylindrical flat bottom vessel, fitted with four baffles placed at 90° around the vessel periphery. The baffle widths were equal to one-tenth of vessel diameter ($d_T/10$). Temperature control of the crystallizer was accomplished by a programmable thermostatic bath provided with a cryostat (*Huber Compatible Control CC3*) with a temperature control accuracy ± 0.01 °C and data acquisition system. All experiments were carried out at constant cooling rate of 6 °C/h from the saturation temperature of 30 °C. During the process concentration changes of borax solution were monitored in line using *Na*-ion selective electrode (ISE). The power consumption was determined using torque meters produced by *Lightnin-LabMaster*. Crystal growth and shape were determined by *Carl Zeiss* optical microscope with an enlargement of 100 times, while the final product of crystallization were sieved to obtain the crystal size distribution by weight.

2.2 Measurement of solubility

The solubility of borax was determined in the range from 3 to 35°C. Saturated borax solutions were prepared by dissolving analytically pure borax decahydrate in ultrapure water. A flask containing the saturated solution and excess solid phase of borax was put into a thermostatically controlled bath, and it was stirred for 6 h to attain equilibrium. After attaining saturation, the equilibrium concentration of borax was determined by volumetric titration with *NaOH* in the presence of mannitol and phenolphthalein as indicators [2,3].

2.3 Measurement of metastable zone width

Supersaturated solutions exhibit a metastable zone, which constitutes the allowable supersaturation level during every crystallization process. Within this metastable zone spontaneous nucleation is not likely to occur. Only by further increase in supersaturation, a certain degree of supersaturation will be reached at which spontaneous nucleation occurs [4]. In this work the metastable zone widths of borax solutions were measured by the conventional polythermal method. A solution with known composition was prepared in accordance with solubility data. The saturated solution was cooled down at a given linear cooling rate until the shower of visible nuclei appeared. Then, this method consists in the determination of the maximum undercooling ΔT_{\max} :

$$\Delta T_{\max} = T_s - T_p \quad (1)$$

where T_s is saturation temperature and T_p is temperature at which the first nuclei have been observed. The difference between these two temperatures is called metastable zone width. The relation of maximum supersaturation to the maximum undercooling can be expressed by the following equation [5,6].

$$\Delta C_{\max} = \left(\frac{dC^*}{dT} \right) \Delta T_{\max} \quad (2)$$

2.4 Measurement of growth rate

During the crystallization process, the crystal slurry was withdrawn from the crystallizer in order to estimate the variation of crystal size against elapsed process time. Slurry was withdrawn using special type of syringe. Sampling point was located above impeller plane ($z/H = 0.8$; $l/(d_T/2) = 0.4$), in the middle plane between adjacent baffles. The withdrawn samples of crystals were sized immediately by microscope with an image analyzer in order to investigate the effect of the impeller position on the overall crystal growth rate.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Solubility and metastable zone width

Fig. 1 shows the solubility curve which indicates that the solubility of borax increases as temperature increases. Solubility data obtained in this work are in very good agreement with those given by *Borax Inc.* [7].

The variations of metastable zone width for different saturation temperatures at four off-bottom impeller clearances are also presented in Fig. 1. The experimental results show that impeller clearances affect the metastability range and however little this effect might be, it could be noticed. The metastable zone width is the widest at $c/H = 0.1$. With increasing off-bottom clearance the metastability range decreases, but it is evident that there is no regular trend. The metastability range is the narrowest at $c/H = 0.3$, while metastable zone widths obtained at position $c/H = 0.4$ and 0.5 are situated between these two previously mentioned values of c/H . Recorded differences between metastable zone widths could be attributed to the hydrodynamic conditions in the system caused by impeller used and its different positions that will be discussed in detail later.

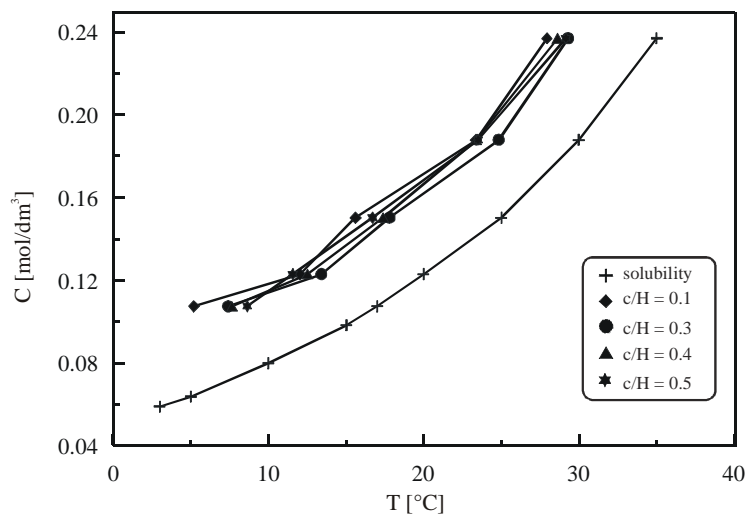


Figure 1. Variation of metastable zone width with off-bottom impeller clearance

3.2 Nucleation

It is well known that the nucleation kinetic is characterized by relationship between the metastable zone width, ΔC_{\max} , and the mass nucleation rate B :

$$B = k_n \Delta C_{\max}^n \quad (3)$$

where k_n is nucleation rate constant and ΔC_{\max} the maximum allowable supersaturation. The exponent n is referred to as apparent order of nucleation. The total rate of nucleation, B , is the sum of the four contributions of different mechanisms:

$$B = B_{\text{hom}} + B_{\text{het}} + B_{\text{sur}} + B_{\text{att}} \quad (4)$$

where B_{hom} , B_{het} , B_{sur} and B_{att} are the rate of homogeneous nucleation, heterogeneous nucleation, secondary surface nucleation, and the rate of attrition induced secondary nucleation. However, one contribution is dominant in a given range of supersaturation [8]. In the unseeded batch cooling crystallizer, the primary nucleation occurs dominantly. Mersmann *et al.* [9,10] suggested a rapid, simple and indirect method to determine the nucleation mechanism in a classical nucleation theory by measuring the degree of supersaturation and solubility at a constant cooling rate. Using this method it was found that the heterogeneous primary nucleation is the dominating mechanism in the examined system. In this case the nucleation rate can be calculated by the following equation:

$$B_{\text{het}} = 0.965 \varphi_{\text{het}} \frac{D_{AB}}{d_m^5} \left(\frac{\Delta C_{\max}}{C_c} \right)^{7/3} \sqrt{f \ln \frac{C_c}{C^*}} \exp \left[-1.19 f \frac{[\ln(C_c / C^*)]^3}{(\eta \ln S)^2} \right] \quad (5)$$

where φ_{het} is the heterogeneity factor and f is the reduction factor for the nucleation work. For heterogeneous nucleation $0 < f < 1$, and depends on the contact angle between the surface of the foreign particles and surface of the nucleus [11]. D_{AB} is a bulk diffusivity ($= 10^{-10}$ m²/s in the low viscous solutions) and $d_m = (C_c / N_A)^{-1/3}$ where N_A is Avogadro number. The calculation was carried out with $D_{AB} = 1 \times 10^{-10}$ m²/s, $C_c = 4.48$ mol/dm³ which was valid for estimated parameters of $\varphi_{\text{het}} = 10^{-11}$ and $f = 0.1$. In our experiment, nuclei may be generated by the heterogeneous primary nucleation that occurs by appearance of "active" particles (heteronuclei) in solution with foreign surfaces (the walls of the vessel, impeller, baffle etc.).

In Table 1 are shown the nucleation rates according to the different off-bottom impeller clearances. The nucleation rate is determined according to equation 5, taking into account the metastable zone width which varies with impeller position in the way previously described.

Table 1. Nucleation rates according to the different off-bottom impeller clearances

c/H	0.1	0.3	0.4	0.5
Nucleation rate (No./m ³ s)	1.406 x10 ¹⁸	20.311x10 ¹⁸	1.375x10 ¹⁸	1.207x10 ¹⁸

It is evident that the nucleation rate was significantly increased when impeller was located at the clearance noted as $c/H = 0.3$. This is a consequence of the fluid-dynamic regime in the

tank generated by the impeller type used and its position. Radial-flow impeller discharges flow toward the wall of the vessel. As the discharge flow impinges on the vessel wall, it splits into two streams near the wall forming two loops in the tank. However, if a radial-flow impeller is sufficiently far from the vessel base, large recirculation flows above and below the impeller are present. The lower flow loop is characterized by weaker impact on the tank bottom. On the other side, if impeller is placed very close to the tank bottom, the lower recirculation flow changes its shape and its characteristics as well. It is plain that SBT impeller positioned at $c/H = 0.3$ provided hydrodynamic conditions in the tank which caused the highest nucleation rate.

3.3 Crystal growth and Crystal size distribution

The mean crystal sizes were measured to investigate the impact of off-bottom impeller clearance on the crystal growth. The overall linear growth rate of crystal at any time t of process [12] can be obtained by the direct measurement of the crystal size, L , and be expressed by

$$G = \frac{L_t - L_{t-1}}{\Delta t} \quad (6)$$

Fig. 2 shows the results of the measured mean crystal sizes according to the batch time at cooling rate of $6\text{ }^\circ\text{C/h}$ and impeller speed of 300 rpm. After nucleation the formed crystals continued to grow causing supersaturation decrease. The example of typical variation of supersaturation ΔC against elapsed time is also shown on the Fig. 2 for $c/H = 0.1$. The crystal size reached an asymptotic value ($\sim 250\text{ }\mu\text{m}$) within 150 minutes. For all impeller clearances examined, the crystal growth behaviors were almost identical. However, regardless of small variations in results can be noticed that the growth behavior at $c/H = 0.1$, in the range of the batch time $t > 150$ minutes, differs from those at other clearances used. The fluid-dynamic regime in which a radial impeller operates at $c/H = 0.1$ is different from the more conventional cases in which the impellers are placed higher in the tank. It was suggested that the suspension of crystals obtained by mixing at this clearance provided the relatively high concentration of settled crystals at the bottom of the crystallizer and produced agglomerated crystals which resulted in larger mean crystal size.

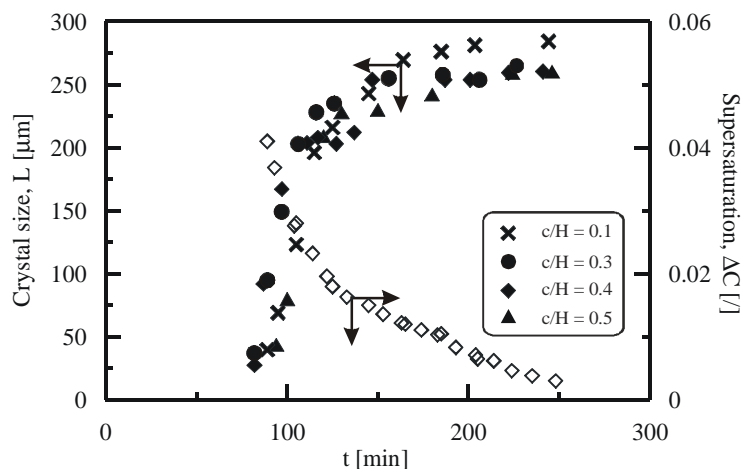


Figure 2. The changes of crystal size and supersaturation ΔC against elapsed time for different off-bottom impeller clearances

The size distributions of product crystal at different off-bottom clearance are presented in Fig. 3. As off-bottom clearance increases, the fraction of smaller crystals does not change much. The distributions show that the fraction of medium crystals increases as off-bottom clearance increases, while the fraction of large crystals decreases. This may indicate that agglomeration took place more frequently for medium size crystals as the off-bottom clearance was increased.

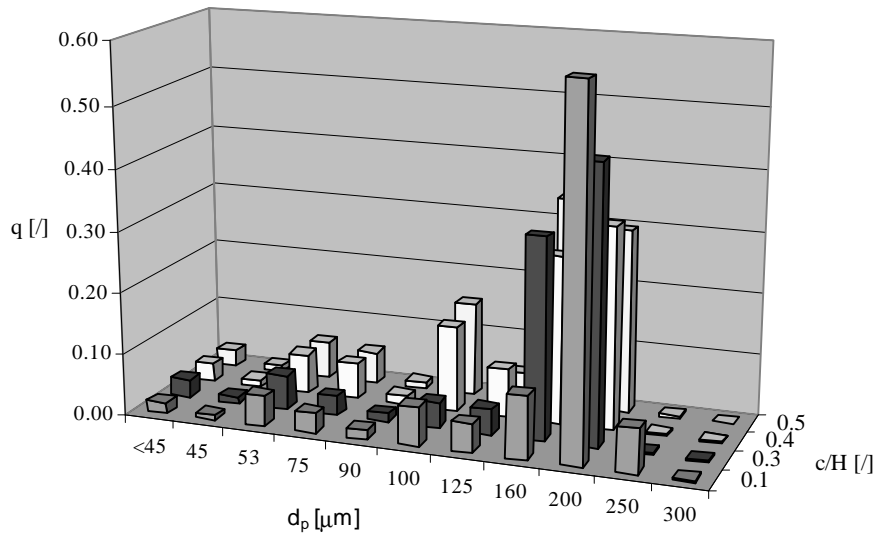


Figure 3. Crystal size distributions for different off-bottom impeller clearances

The photographs of the final products of borax crystals obtained with an optical microscope at various off-bottom impeller clearances are given in Fig. 4.

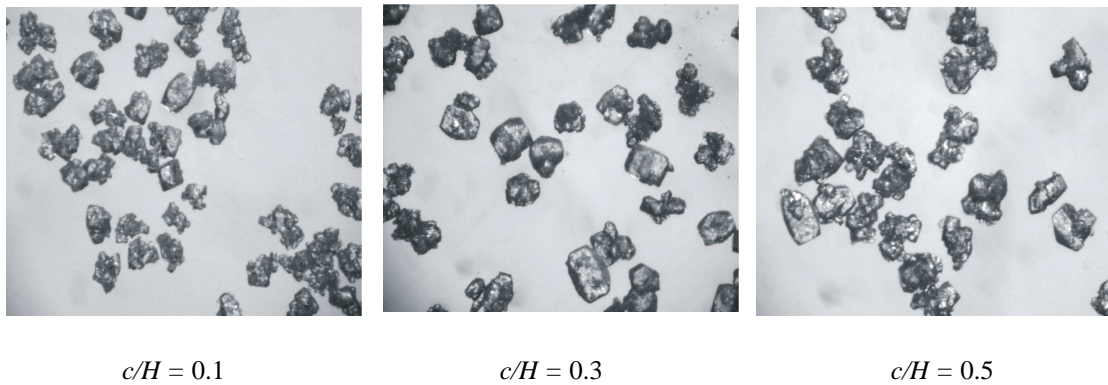


Figure 4. Photographs of crystals obtained at different off-bottom impeller clearances

It is evident that in an agitated batch crystallizer the nucleation rate as well as crystal growth and crystal size distribution are significantly influenced by the hydrodynamic regime in the system. Working with the SBT radial impeller at different off-bottom clearances and using VisiMix 2000 Turbulent program have been observed different liquid flow patterns during the flow visualization experiments (Fig. 5). When the stirrer is set rather far from the

vessel bottom ($c/H = 0.3$) two well-defined ring vortices, above and below the impeller, persist in the vessel. Two loops were also noticed in the system when the impeller clearances were $c/H = 0.4$ or 0.5 . At these values of ratio c/H the lower loop has a less pronounced impact on the vessel bottom than at impeller position noted as $c/H = 0.3$. Because of weaker mixing efficiency close to the tank bottom, particles have a tendency to cluster together. The results therefore, indicate that a further increase in the clearance would be absolutely counter-productive.

When the stirrer is close to the bottom ($c/H = 0.1$) the lower vortices are almost absent, i.e. the flow undergoes a transition from the standard double loop pattern to one with impeller stream directed downwards [13,14]. In this case, the bulk flow near the vessel bottom is directed from the stirrer to the periheral zone near the wall where the solid particles tend to accumulate. Thus, in this zone there exists some kind of "forced" agglomeration.

If the aim of process requires larger, more uniform and less agglomerated crystals of borax off-bottom impeller clearance of $c/H = 0.3$ may be considered as a more viable option under present experimental conditions.

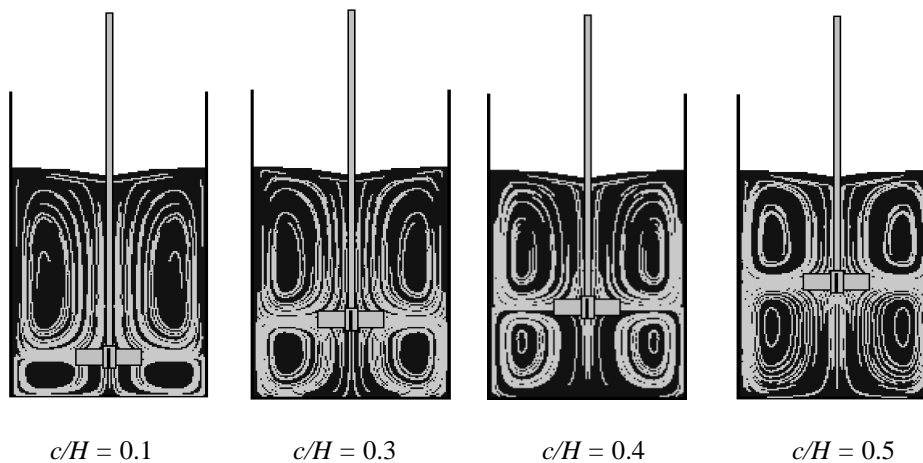


Figure 5. Simulations of flow pattern in crystallizer at various values of c/H

3.3 Power consumption

Torque measurements were performed for all off-bottom impeller clearances examined. Since the crystallization is process in which a new, solid phase forms from supersaturated solution, a data acquisition software package was used to evident the possible changes of power consumption during the process. In this work the power consumption is expressed in terms of power consumption per unit mass of suspension.

From Fig. 6 can be seen that values of (P/m) are almost constant with an increase of the off-bottom impeller clearance. The obtained results also indicated that values of this parameter do not change significantly over the process time. Obviously, presented results can not be taken for granted, because experiments in this work were carried out in crystallizer of relatively small volume. These effects should be studied further in greater detail employing experimental units of larger scale. Namely, for the scale-up of crystallization process the power input is of fundamental interest.

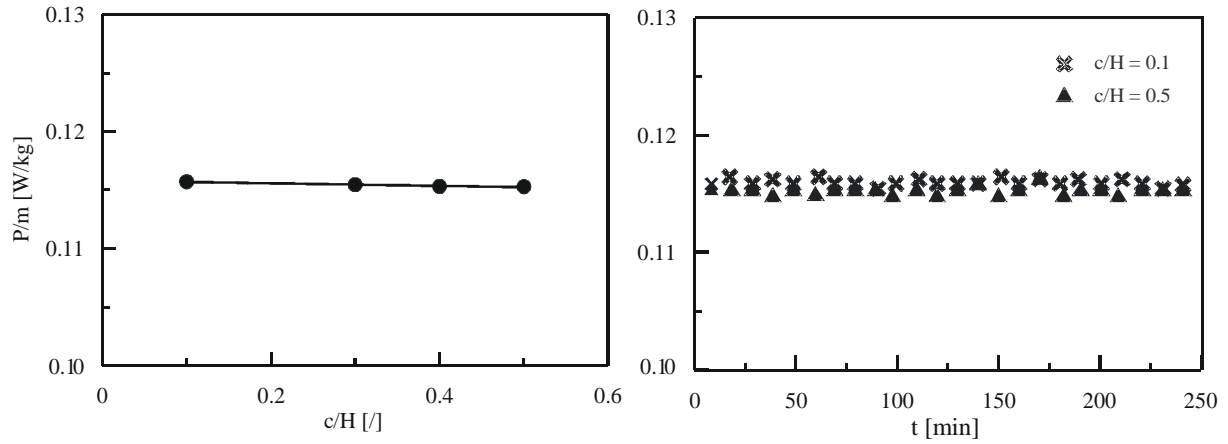


Figure 6. (P/m) vs. (c/H) and (P/m) vs. process time

4. CONCLUSIONS

In an agitated batch crystallizer metastable zone width, nucleation rate, crystal growth as well as crystal size distribution are significantly influenced by hydrodynamic regime in the system determined by impeller used and its position. The experimental results show that off-bottom impeller clearances affect the metastability range and however little this effect might be it could be noticed.

Using Mersmann's criterion to determine the nucleation mechanism, it was found that the heterogeneous primary nucleation is the dominating mechanism in this work. In our experiment, nuclei may be generated by the heterogeneous primary nucleation that occurs by heteronuclei in solution with foreign surfaces. SBT impeller positioned at $c/H = 0.3$ provided hydrodynamic conditions in the tank which caused the highest nucleation rate.

On the basis of the experimental results and observations shown above, the impact of impeller clearance on the crystal size distribution in the product line is an important factor that should be taken into account. If the aim of process requires larger, more uniform and less agglomerated crystals of borax off-bottom impeller clearance of $c/H = 0.3$ may be considered as a more viable option under present experimental conditions.

In the examined system the values of (P/m) do not change significantly at different off-bottom impeller clearances. The obtained results also indicated that values of this parameter are nearly constant over time, so they do not change during the process of crystallization regardless of the fact that during process the new solid phase forms.

5. NOMENCLATURES

B	total rate of nucleation, No./m ³ s	D	impeller diameter, m
c	off-bottom clearance, m	G	overall linear crystal growth rate, m/s
C	solution concentration, kmol/m ³	H	height of liquid from tank bottom, m
C_c	crystal molar density, kmol/m ³	l	radial sampling position from the tank wall, m
C^*	solubility, kmol/m ³	L	crystal size, m
ΔC	supersaturation, kmol/m ³	m	suspension mass, kg
ΔC_{max}	maximum supersaturation, kmol/m ³	N	impeller speed, rps or rpm
d_p	particle size, μm	q	mass fraction, /
d_T	tank diameter, m		

(P/m)	power consumption per unit mass (W/kg)	z	axial sampling position from the tank bottom, m
S	relative supersaturation, /	η	number of ions per molecule
t	process time, min		
T	temperature, °C		
T_s	saturation temperature, °C		
ΔT_{\max}	maximum available undercooling, °C		

6. REFERENCES

1. Shimizu K., Nagasawa H., Takahashi K., 1995. "Effect of off-bottom clearance of a turbine type impeller on crystal size distribution of aluminum potassium sulfate in a batch crystallizer", *J. Crystal Growth*, **154**, 113-117.
2. Braman, R.S., 1968. "Boron Determination" in: *Encyclopedia of Industrial Chemical Analysis, Vol. VII*, Eds. Interscience Publisher, New York, pp. 405-409.
3. Yildiz Yuksel G., Titiz S., Bulutcu A.N., 1996. "Solubility of sodium perborate tetrahydrate in water and sodium metaborate solution", *J. Chem. Eng. Data*, **41**, 586-588.
4. Ulrich J., Strege C., 2002. "Some aspects of the importance of metastable zone width and nucleation in industrial crystallizers", *J. Crystal Growth*, **237-239**, 2130-2135.
5. Mulin J.W., 2004. *Crystallization, 4th edit.*, Elsevier, Amsterdam.
6. Gurbuz H., Ozdemir B., 2003. "Experimental determination of the metastable zone width of borax decahydrate by ultrasonic velocity measurement", *J. Crystal Growth*, **252**, 343-349.
7. <http://www.borax.com>
8. Kim K.J., Mersmann A., 2001. "Estimation of metastable zone width in different nucleation processes", *Chem. Eng. Sci.* **56**, 2315-2324.
9. Mersmann, A.M., Angerhofer M., Gutwald T., Sangl R., Wang S., 1992. "General prediction of median crystal sizes", *Separations Technology*, **2**, 85-97.
10. Cheon Y.H., Kim K.J., Kim S.H., 2005. "A study on crystallization kinetics of pentaerythritol in a batch cooling crystallizer", *Chem. Eng. Sci.* **60**, 4791-4802.
11. Kim Y.H., Lee K., Koo K.K., Shul Y.G., Haam S., 2002. "Comparison study of mixing effect on batch cooling crystallization of 3-nitro-1,2,4-triazol-5-one (NTO) using mechanical stirrer and ultrasound irradiation", *Cryst. Res. Technol.* **37**, 928-944.
12. Cheon Y.H., Kim K.J., Kim S.H., 2005. "A study on crystallization kinetics of pentaerythritol in a batch cooling crystallizer", *Chem. Eng. Sci.* **60**, 4791-4802.
13. Montante G., Lee K.C., Brucato A., Yianneskis M., 1999. "An experimental study of double to-single loop transition in stirred vessels", *Can. J. Chem. Eng.* **77**, 649-659.
14. Conti B., Gianetto A., 1986. "Solid agitation and mixing in aqueous systems", in: *Encyclopedia of Fluid Mechanics, Vol. II* (N.P. Cheremisinoff, ed) Chapter 31, Gulf Publishing Co., Houston, pp. 886-900.