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Effect of Impeller Off-bottom Clearance on Crystal Growth Kinetics of Borax in Dual-impeller Batch Cooling Crystallizer

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The aim of this work was to experimentally investigate the influence of impeller off-bottom clearance on crystal growth kinetics of disodium tetraborate decahydrate (borax) in a dual-impeller batch cooling crystallizer. Examinations were carried out in a crystallizer of 15 dm^3 with liquid height to crystallizer diameter ratio (H/d_T) of 1.3. In this research, two pitched blade turbines (PBT) with diameter D/d_T=0.33, were mounted on the same shaft with a constant spacing between impellers (s/D=1.0). Mixing was performed at the impeller speed which ensured the state of complete suspension in the system (N=N_{JS}). The impeller off-bottom clearance (C/D) was varied from 0.2 to 1.3. Crystallization was carried out by a controlled cooling of the solution saturated at 30°C. Concentration of the solution was measured in line by potentiometric method, while the changes of crystal size over time were determined by optical microscope and image analysis software.
Experimental results indicate that impeller off-bottom clearance influences the change of crystal size over process time. At all examined impeller off-bottom clearances, crystal growth is integration limited. The value of an order of crystal growth rate changes insignificantly with C/D ratio, while the crystal growth rate constant is affected by the change in hydrodynamics. Obtained results are a consequence of the hydrodynamic conditions in the dual-impeller crystallizer. In order to analyse the overall fluid flow pattern, in which an interaction of the flows generated by each of the impellers occurred, photographs of the flows were taken and simulations by VisiMix 2000 Turbulent were made. Taking into account the values of kinetic parameters of crystal growth, characteristic of obtained crystals, power consumption and the overall fluid flow pattern, it is possible to define the impact of impeller off-bottom clearance on borax crystal growth kinetics.

1. Introduction

Crystallization as a solid-liquid separation process usually takes place in suspension and it can be conducted batch wise in the vessel equipped with stirrer operating in the turbulent regime. For this reason it is dependent on the fluid flow structure in the vessel which in turn is highly influenced by an impeller configuration. The impellers inside the mixing tank can be used in different configurations, i.e. the system can be single, dual or multiple impeller system. The type of this configuration depends on the liquid high to vessel diameter ratio. If it exceeds the value of 1.2 a second or more impellers should be mounted in the same shaft in order to avoid the formation of stagnant zone in the mixing system.
Many researchers have pointed out that circulation inside a stirred tank could be influenced by mixing parameters such as impeller speed, diameter and position in both single- and multi-impeller systems. Most of the research carried out on two impeller systems has been involved with gas dispersion and suspension of inert particles in water while the study which investigates the influence of mixing in dual impeller system on crystallization process is very few. The aim of this work was investigate the influence of impeller-off bottom clearance in dual impeller crystallizer on borax decahydrate ($Na_2B_40_7{\cdot}10\ H_20$) crystal growth kinetics in the process of batch cooling crystallization. This compound presents the refined form of natural sodium borate. It is widely used in the production of borosilicate glasses, glass wool, ceramics, detergents, fire proof materials, etc. Since crystallization is an important step in the process of its production to its refined form, in order to produce crystals of borax with a specified purity and crystal size distribution at minimum cost, it is necessary to operate the crystallizer at the optimum conditions (Gurbuz et al., 2003).

2. Materials and methods

All experiments were performed in a laboratory-scale stirred batch cooling crystallizer with a volume of 15 dm^3 described in details in previously published paper (Kaćunić et al., 2016). The crystallizer was a cylindrical flat bottom vessel made of plexiglas with an internal diameter of 0.24 m. The vessel was equipped with four baffles placed at 90^o around the vessel periphery. The ratio of liquid height to tank diameter (H/d_T) was 1.3 what allowed an introduction of a second impeller on the same shaft in the examined system. Mixing was performed by two pitched blade turbines (PBT) mounted on the same shaft. Impeller to tank diameter ratio (D/d_T) was 0.33 while the spacing between the impellers, s, was set to s/D =1. In order to examine the influence of off-bottom clearance on crystal growth kinetics of borax, its value, expressed by a dimensionless ratio C/D, was varied in range from 0.2 to 1.3.

At all examined conditions mixing was performed at just-suspended impeller speed, N_{JS}. The values of N_{JS} were determined using a visual 0.9H method according to Einenkel and Mersmann. This method defines the N_{JS} as the speed at which the cloud of suspension reaches 0.9 of the total liquid height. Measurements were performed in a mother liquor saturated at 30°C in which 598 g of borax crystals (x_p = 275 μm) was suspended. This mass was calculated from theoretical crystal yield, while their size presents the largest granulometric class of borax obtained in preliminary experiments.

During the process, the change of borax solution concentration was monitored in-line by the means of the sodium polymer membrane ion-selective electrode (*Na-ISE*) with a measuring range from 1 to 10^{-6} mol/dm^3 and *Metrohm 913 pH Meter*. Details about ISE application were explained in previously published paper (Kaćunić al., 2013). Temperature control of the crystallizer was accomplished by a programmable thermostatic bath (*Medingen TC 250*) and an appropriate data acquisition system. The power consumption was determined using torque meters produced by S. Himmelstein and Company.

Aqueous solution of borax saturated at 30 °C was cooled at a constant cooling rate of 6 °C h^{-1}. After the onset of nucleation, the crystal slurry was periodically withdrawn from the crystallizer in order to determine the change in size of the growing crystals against process time at examined conditions. Slurry was withdrawn always from the same place in the crystallizer using a syringe. Sampling point (d_s, h_s) was located above the impeller plane (d_s/d_T = 0.458; h_s/H = 0.753), in the middle plane between the adjacent baffles. At the end of the process crystal size distribution of obtained products was measured by a laser diffraction particle size analyser (*Horiba LA-300*)**.** Crystal agglomeration of the final product was analysed using a *Carl Zeiss* optical microscope with a magnification of 100 times.

To determine the flow patterns in the mixing tank at different PBT-PBT off-bottom clearances, a streak photography based on the work of Ibrahim and Nienow (1995) was used. All pictures were taken in the dark room. A 1500 W halogen lamp was used as a source of light to illuminate a vertical section of the tank. The light passed through two parallel vertical slits, 5 mm wide. Tracers used to aid flow visualization were crystals of borax decahydrate with an average size of 275 μm, placed in a solution saturated at 30 °C.

3. Experimental results and discussion

3.1 Influence of impeller off-bottom clearance on just suspended impeller speed and power consumption

In this work the state of complete suspension was achieved at that value just suspended impeller speed (N_{JS}) at which the cloud of suspension reached 90 % of the liquid height. Under these conditions Zwietering's criterion for N_{JS}, where no particles are left stationary at the bottom of the tank for more than 1 or 2 s, was satisfied as well.

From Figure 1 it is clear that with an increment of impeller off-bottom clearance, just suspended impeller speed increases. This result is a consequence of different hydrodynamic conditions generated in the crystallizer equipped with two PBT impellers due to changes of impellers off-bottom clearance.

Generally, flow pattern of a PBT impeller can be divided into three regions: (I.) high speed flow below the impeller, (II.) cone shaped zone below the impeller, characterized by low fluid velocities and (III.) the rest of the vessel (Rewatkar and Joshi, 1991). High speed flow creates a primary circulation loop, while the cone shaped region bellow the impeller presents a minor recirculation loop. In a PBT dual impeller system, each of the impellers generates its own flow. When the spacing between them is set to the ratio s/D=1, an interaction of flows developed by each impeller is present. When lower impeller is placed close to the vessel base (C/D=0.2), the flow of the lower impeller cannot be completely developed but high liquid velocity present in the impeller region, acts on the settled crystals and lifts them from the bottom even at lower rotational speeds. Crystals swept from the base by the lower impeller discharge stream are then lifted to the 0.9 H by the upper impeller stream (Figure 2a.) As the impeller off-bottom clearance increases, a cone shaped zone below the impeller is broadening; liquid velocities in a high speed zone reach the crystallizer base only when the impeller

speed is increased. Although flows generated by both of the impellers act in suspension of the crystals, the flow of the lower one is more responsible for lifting of the settling crystals from the bottom.

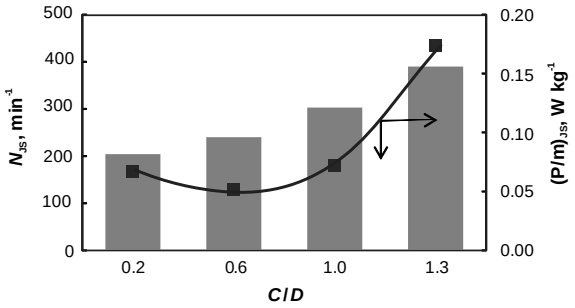

Figure 1: Influence of impeller off-bottom clearance on N_{JS} and power consumption.

From the value of N_{JS} and torque, power consumption was determined as well. The influence of impeller off-bottom clearance on power consumption expressed in terms of power consumption per unit mass as $(P/m)_{JS}$ is shown in Figure 2. From the figure it is obvious that power consumption is significantly dependent on just suspended impeller speed; it increases as the impeller speed increases.

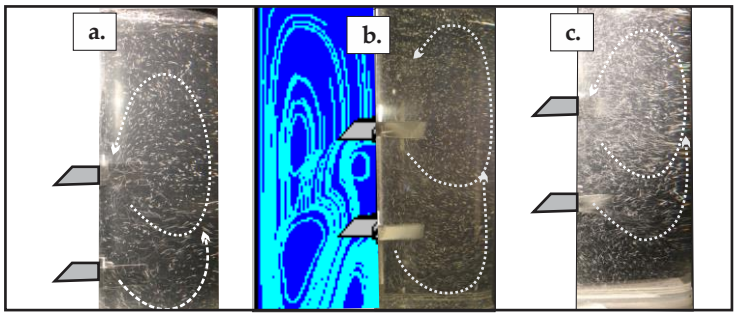

Figure 2: Flow-pattern images obtained at: a) C/D= 0.2; b) C/D=1.0; d) C/D=1.3

Information on power consumption in examined mixing systems can facilitate a selection of mixing conditions. To estimate the optimum mixing parameters in the process of crystallization, the effect of the flow pattern on crystal growth kinetics and properties of crystal product must be taken into consideration.

3.2 Influence of impeller off-bottom clearance on crystal growth kinetics

In order to analyse the influence of hydrodynamic conditions generated at different impeller off-bottom clearances in a dual PBT impeller crystallizer on crystal growth, a change of the average crystal size over process time was determined. For that reason linear crystal size, L, of the growing crystals was determined by measurement of the largest linear size, L_c, of n = 50 largest regularly shaped crystals. This was done by sampling of the slurry in regular time intervals. Average crystal size was calculated by equation:

$$L = \frac{L_c}{n} \tag{1}$$

The change in linear crystal size over process time for all examined conditions is presented in Figure 3a. Since the driving force of crystal growth is supersaturation of the mother liquor, a typical change of supersaturation, which occurs simultaneously, is shown in the same figure and it is expressed in terms of absolute supersaturation, Δc.

In an unseeded batch cooling crystallization, crystal growth begins after nucleation. In the beginning of the growing process, an intensive enlargement of the crystal size is accompanied by an intensive decrement of the supersaturation, but after a definite time, a change in both values becomes less pronounced. Regarding the intensity of change in crystal size, crystal growth can be divided in two periods; a period of an intensive growth and a period of slow crystal growth. Actually, time dependent change in crystal size is a consequence not only of crystal growth but also of parallel processes which occur in the crystallizer, such as breakage and agglomeration. In these analyses of crystal size, only regularly shaped crystals were sized and the impact of

agglomeration was omitted. Due to an intensive enlargement of crystal size in the first period of the growing process, it could be assumed that crystal growth was dominant but when crystals reached a certain size (about 160 μm), a significantly lowered increment of crystal size indicates that breakage of the crystals, due to the crystal/impeller and crystal/crystal collision took place as well.

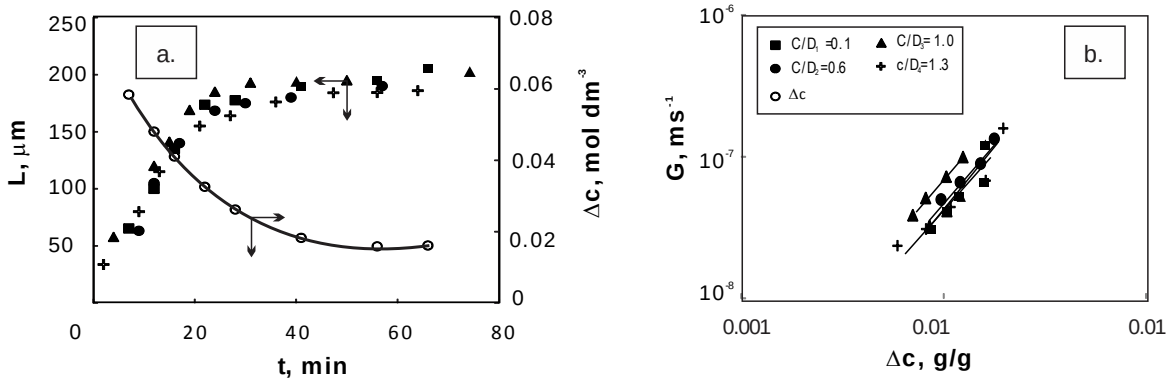

Figure 3: a) Variation of crystal size over process time at different impeller off-bottom clearances; b) Growth rates of borax as a function of supersaturation at different C/D ratio.

In order to analyse the influence of hydrodynamic conditions on crystal growth, using the on crystal size over process time shown in Figure3, linear crystal growth rate for the first period of the growing process was calculated according to equation:

$$G = \frac{dL}{dt} \tag{2}$$

Calculated growth rates were presented as a function of supersaturation expressed in mass fractions (Figure 3b). From Figure 3b it is obvious that for all impeller off-bottom clearances, crystal growth rate increases with supersaturation. At all supersaturation values, crystal growth rate is the highest when *C*/*D*=1 while at other positions its values are very close. Presented crystal growth rates for examined off-bottom clearances are afterward expressed as function of supersaturation (Table 1), according to the overall crystal growth rate equation:

$$G = k_G \Delta c^g \tag{3}$$

where *G* is the overall linear crystal growth rate, k_G presents the overall crystal growth rate constant and *g* is the order of crystal growth rate.

Table 1: The equation of overall growth rates at different dual PBT impeller off-bottom clearances.

C/D	0.2	0.6	1.0	1.3
G	$G = 8.2 \cdot 10^{-5} \Delta c^{1.68}$	$G = 9.5 \cdot 10^{-5} \Delta c^{1.65}$	$G = 1.4 \cdot 10^{-4} \Delta c^{1.63}$	$G = 8.9 \cdot 10^{-5} \Delta c^{1.55}$

From equations of crystal growth rates presented in table 1, it was possible to estimate the value of kinetic parameters. Constant k_g depends on crystal/mother liquor relative velocity while *g* is the supersaturation order of crystal growth rate (Omar and Urlich, 2003). It was found that the values of parameter *g* range from 1.55 to 1.68 and the value of parameter k_g ranges from 8.2 to 14 $\cdot 10^{-5}$ m s^{-1} and it is the highest at *C/D* = 1.0, while its value at other examined positions was very similar.

The values of crystal growth rate constant are obviously consequence of the overall fluid flow inside the crystallizer which changes with impellers clearances. As previously stated, when lower impeller is positioned close to the vessel base its flow cannot be fully developed. An increase of impeller off-bottom clearance to *C*/*D* = 0.6 and *C*/*D* =1.0 results in a complete formation of the flow of the lower PBT impeller. At these positions, discharge streams of both of the impellers are directed from the lower surface of impellers blades towards the tank base, whereupon the stream of the lower one goes up the side of the vessel wall. In the middle of the liquid height this stream meets a discharged stream of the upper impeller; they merge and proceed to the liquid surface. This way, a system strong circulation loop, occupying a large volume of the vessel is formed in a dual impeller system (Figure 3b.). Even though the value of Reynolds number in system with *C*/*D* =1.0 is lower than the one at *C*/*D* = 1.3, described circulation loop enhanced the conditions for mass and heat transfer inside the whole tank.

The growth of crystals is considered to be a two-step process; volume diffusion is followed by surface integration of the solute to the crystal lattice (Mersmann et al., 1994). Clearly, the growth rate is limited by the slower step. To estimate the controlling step during the growth of borax crystals at different off-bottom clearances of dual PBT system, a diagram of dimensionless crystal growth rate ($G/2k_d$) vs. dimensionless supersaturation ($\Delta c/c_c$) was used (Figure 4).

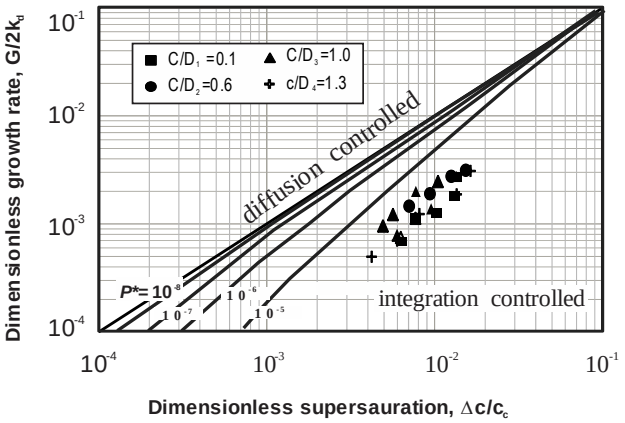

Figure 4: Dimensionless growth rate vs. dimensionless supersaturation

The factor *P** in diagrams presents a curve fitted to the crystal growth data at which the two mechanism of the crystal growth are superimposed. The value of the crystalizing parameter *P** can be calculated according to the equation (Mersmann, 1995):

$$P^* = \frac{k_d d_m}{D_{AB}} \left(\frac{c^*}{c_c}\right)^{0.75} \ln\left(\frac{c_c}{c^*}\right) \tag{4}$$

where k_d is the mass transfer coefficient, d_m is molecular diameter [$d_m = (c_c/N_A)^{-1/3}$] where N_A is the Avogadro number, c^* is the solubility, c_c is the molar density while D_{AB} present the volume diffusion coefficient. Volume diffusion coefficient was calculated by Stokes-Einstein equation:

$$D_{AB} = \frac{k_B T}{3\pi\eta_L \ln d_m} \tag{5}$$

In this equation, $k_B = 1.38 \cdot 10^{-13}$ JK^{-1} is the Bolzman konstant, T is the absolute temperature, and η_L is dynamic viscosity of the solution.
According to Herndl (1982), the mass transfer coefficient, k_d, in a stirred vessel ($0 \le N_{RE} \le 10^5$) can be calculated using the volume diffusion coefficient D_{AB} and the Schmidt number ($Sc = \eta_L/D_{AB}$):

$$k_d(L) = \frac{D_{AB}}{L}\left[0.8\left(\frac{\varepsilon \cdot L^4}{\eta_L^3}\right)^{0.2}\left(\frac{\eta_L}{D_{AB}}\right)^{0.33} + 2\right] \tag{6}$$

where ε is the mean specific power input which can be expressed by (Mersmann, 1994):

$$\varepsilon = \frac{4P_0}{\pi} N^3 D^2 \left(\frac{D}{d_T}\right)^2 \frac{d_T}{H} \tag{7}$$

where P_0, is the power number. The values of P_0 for dual PBT impeller system at *C*/*D* ratios are calculated from power consumption. The values of parameter P^* at different off-bottom clearances are ranging from 10^{-6} to 10^{-5}. Since experimentally determined values of the crystal growth rate are below the $P^*=10^{-5}$ curve, it suggests that the crystal growth rate is integration limited in all examined systems.

3.3 Influence of impeller off-bottom clearance on product size

At the end of the experimental runs, a weight mean crystal size, x_c, of the product was determined by laser diffraction. This value is obtained from the mass percentage of crystals in the classes of defined size in the range from 45 to 300 μm. From the values listed in table 2, it is clear that an increase of impellers off-bottom clearances results in a decrease of mean crystal size.

Table 2: Weight mean crystal size at examined dual PBT impeller off-bottom clearances.

C/D	0.2	0.6	1.0	1.3
x_c, μm	216	214	195	175

This phenomenon can easily be explained if the overall fluid flow structure inside a crystallizer is considered. In the systems with 0.2<*C*/*D*<0.6 crystals are larger and significantly more agglomerated. At these conditions circulation inside crystallizer is limited inside lower part of suspension volume. Along with the lower value of Re number formed circulation doesn't occupied the zone above upper impeller, where the mixing is rather poor and crystal agglomeration took a place. On the other hand, crystals of borax obtained at *C*/*D* = 1.3 were smaller. As previously explained, at this position (*C*/*D*=1.3) a reverse circulation loop bellow the lower impeller broadens and the primary circulation stream hardly reaches the vessel base. Despite highest value of Re overall circulation in the crystallizer is lower compering to *C*/*D*=1.0 what eventually reflected on the size of crystal product.

4. Conclusions

Impeller off-bottom clearance in a dual PBT impeller system significantly influences hydrodynamic conditions inside the crystallizer. As a consequence of these conditions the state of complete suspension is achieved at different impeller speeds.

Obtained data implies that crystal growth is integration limited in all examined systems. However, the crystal growth rate is higher when flows of both of the impellers is fully developed (*C/D*=1.0) for this ensures good circulation in the crystallizer. Off-bottom clearance reflects on the properties of the borax product as well. This investigation showed that the lower off-bottom clearances result in formation of larger but agglomerated crystals while the increased ones causing smaller size of crystal product.

Acknowledgments

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