Journal of Crystal Growth 312 (2010) 3603–3608

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Effect of mixing on the crystal size distribution of borax decahydrate in a batch cooling crystallizer

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ARTICLE INFO

Article history:
Received 22 July 2009
Received in revised form
24 May 2010
Accepted 8 September 2010
Communicated by J.B. Mullin
Available online 25 September 2010

Keywords:
A1. Solubility
A1. Stirring
A2. Growth from solution
A2. Industrial crystallization
B1. Borates

ABSTRACT

The effect of the impeller speed upon the metastable zone width, supersaturation level, crystal growth and the crystal size distribution of borax decahydrate have been investigated to find operating conditions of a batch cooling crystallizer. The importance of impeller speed was studied in baffled stirred crystallizer with a volume of about 2 dm^3, equipped with four straight blade turbine (4-SBT) cooling at a constant cooling rate. The metastable zone width was determined by visual method, while concentration changes during the process were monitored in line using ion-selective electrode. The crystal size distribution was determined by optical microscope and sieve analysis respectively. The power consumption measurements were performed for all impeller speeds examined as well. On the basis of the experimental results and observations it is evident that in an agitated batch crystallizer the above mentioned parameters are significantly influenced by hydrodynamic regime in the system determined by impeller used and its revolution speed.

1. Introduction

Crystallization is one of the powerful methods for separation and purification in many domains, such as chemical, pharmaceutical and food industries. Agitated vessels are most commonly used equipment in industrial crystallization, and it has been well known that the mixing has dramatic effect on the properties of the product, including crystal size distribution (CSD), purity, morphology and polymorphic form [1,2]. Unfortunately, in many processes of pharmaceutical or chemical industry, crystallizations are carried out in stirred vessels without any optimization of the hydrodynamic conditions, even if, sometimes, these mechanisms are the controlling steps for an efficient separation of the crystals from the liquor and for a suitable morphology of the final product [3].

The purpose of the present work is to investigate the effect of mixing on the borax decahydrate ($Na_2B_4O_7 \times 10\ H_2O$) crystallization in a batch cooling crystallizer. Borax is a product of great industrial interest. It presents the refined form of natural sodium borate used widely in detergent and cleaning formulations, as fungicide, disinfectant or herbicide. It has important role as an agent that modifies the structure of glasses, especially in the production of ultra thin screens, etc. In order to produce crystals of borax with a specified purity and CSD at minimum cost, it is necessary to operate the crystallizer at the optimum mixing conditions [4–6]. Mechanical stirred system equipped with a straight blade turbine (4-SBT) in the vessel with a flat bottom was used during experimental procedure. Different impeller speeds were adopted in batch crystallization, and the effect upon the size distribution of the product crystals was investigated thoroughly.

2. Experimental procedure

The experimental set-up is shown schematically in Fig. 1. All experiments were performed in a laboratory-scale stirred batch cooling crystallizer with a volume of 2 dm^3. The crystallizer was the cylindrical flat bottom vessel with internal diameter of 0.14 m. The vessel was fitted with four baffles placed at 90° around the vessel periphery. The baffle widths were equal to one-tenth of vessel diameter ($d_T/10$). The solution was stirred by straight blade turbine ($D/d_T = 0.45$; number of blades—4; blade width—$0.12D$). The clearance of the impeller from the tank bottom was fixed to $C = 1/3H$. Temperature control of the crystallizer was accomplished by a programmable thermostatic bath (Huber Compatible Control CC 3) with a temperature control accuracy × 0.01 °C and data acquisition system. All experiments were carried out at the constant cooling rate of 6 $^\circ C\ h^{-1}$. During the process concentration changes of borax solution were monitored in line using Na-ion selective electrode (ISE). The measurements were restricted to temperature below 35 °C in order to avoid any decomposition phenomena and problems

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doi:10.1016/j.jcrysgro.2010.09.023

Nomenclature

C	off-bottom clearance (m)
c	solution concentration (mol dm^{-3})
c^*	solubility (mol dm^{-3})
Δc	supersaturation (mol dm^{-3})
$\Delta c_{\max}$	maximum supersaturation (mol dm^{-3})
x	particle size (μm)
x_m	mean particle size defined by Eq. (4) (μm)
d_T	tank diameter (m)
D	impeller diameter (m)
H	height of liquid from tank bottom (m)
l	radial sampling position from the tank wall (m)
m	suspension mass (kg)
N	impeller speed (rps or rpm)
$Q_r(x)$	cumulative frequency function (–)
r	type of quantity of particles (r=0—particle number; r=3—mass or volume of particle)
(P/m)	power consumption per unit mass (W kg^{-1})
t	process time (min)
T	temperature (°C)
T_s	saturation temperature (°C)
Y	product yield (wt%)
$\Delta T_{\max}$	maximum available undercooling (°C)
z	axial sampling position from the tank bottom (m)
ρ_L	density of suspension (kg m^{-3})
σ	standard deviation defined by Eq. (5) (–)

connected with operating mode of ISE as well. The power consumption was determined using torque meters produced by Lightnin-LabMaster. After crystallization for a definite time, the crystals were filtered from the residual solution, and then were dried overnight in air at room temperature in order to measure crystal size distribution. The crystal size distributions were determined by sieve analysis and optical microscope.

2.1. 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 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 [7].

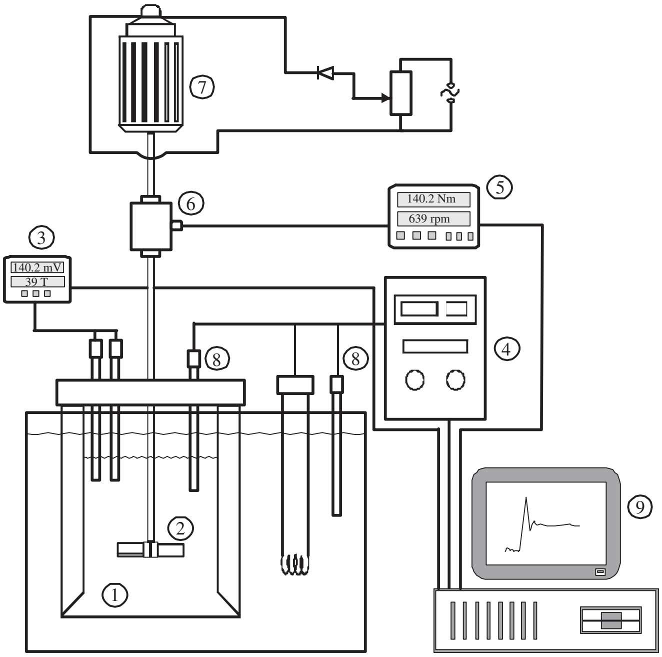

Fig. 1. Experimental set-up: (1) crystallizer, (2) impeller, (3) system for concentration measurement, (4) programmable thermostat, (5) torquemeter, (6) torque sensor and velocity transducer, (7) variable speed motor, (8) temperature probes and (9) computer.

2.2. Measurement of metastable zone width

The metastable zone widths of borax solutions were measured by the conventional polythermal method [8]. 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 $\Delta T_{\max}$

$$\Delta T_{\max} = T_s - T_p \tag{1}$$

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 equations [9,10]:

$$\Delta c_{\max} = \left(\frac{dc^*}{dT}\right)\Delta T_{\max} \tag{2}$$

2.3. Measurement of growth rate and crystal size distribution

During the crystallization, 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 a special type of syringe, always from the same place. Sampling point was located above the 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 microscopy technique with an image analyzer (Motic Images Plus 2.0) in order to investigate the effect of the impeller speed on the overall crystal growth rate.

The size distributions of final products of crystallization were determined by sieve analysis. Sieving of dry solid sample was performed with sieves of 45–300 μm aperture. Experimentally determined CSD is also presented by well-defined mathematical law. Gauss-normal distribution (*GN*) has been found very useful in describing particulate systems analyzed in this work. The expression representing *GN* function on a weight basis is [11,12]

$$\frac{dQ_3(x)}{dx} = \frac{1}{\sigma\sqrt{2\pi}}\exp^{-(x-x_m)^2/2\sigma^2} \tag{3}$$

In Eq. (3), the mean size is defined as

$$x_m = \frac{\Sigma x \Delta Q_3(x)}{\Sigma \Delta Q_3(x)} \tag{4}$$

and standard deviation, σ, is defined as

$$\sigma = \sqrt{\frac{\Sigma (x-x_m)^2 \Delta Q_3(x)}{\Sigma \Delta Q_3(x)}} \tag{5}$$