CI&CEQ

Available on line at
Association of the Chemical Engineers of Serbia AChE
www.ache.org.rs/CICEQ

Chemical Industry & Chemical Engineering Quarterly 18 (4) 547–553 (2012) CI&CEQ

GAYE Ö. ÇAKAL

National Boron Research Institute, BOREN, Ankara, Turkey

SCIENTIFIC PAPER

UDC 661.847:661.847.2:544.4

DOI 10.2298/CICEQ120224031C

PRODUCTION OF FINE ZINC BORATE IN INDUSTRIAL SCALE

In this study, zinc borate production in an industrial scale batch reactor was carried out at the optimum process conditions, determined in the previous studies performed at the laboratory and pilot scale reactors. The production was done via the heterogeneous reaction of boric acid and zinc oxide. The samples were characterized by chemical analysis, XRD, TGA, SEM and particle size distribution. The final product which was obtained in the industrial scale reactor was $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$. The kinetic data for the zinc borate production reaction fit to a modified logistic model where the lag time was taken into account. As observed, the reaction time was influenced by scaling up. There was a lag time of 120 min for the industrial scale production and thus, the reaction completion time was 70 min longer compared to pilot scale. It should be emphasized that the specific reaction rate, k, as well as the average particle size and the hydration temperature of zinc borate were unaffected by scale up.

Keywords: zinc borate; scale up; industrial production; kinetics; logistic model; crystallites.

The world market for flame retardants was estimated at 1.8 Mt in 2007, with the USA accounting for over a third of total demand. Zinc borates account for only a small part of the total flame retardant market. World consumption of zinc borates is estimated in the region of 50,000 t in 2008 [1]. In relation to forthcoming regulations, the use of halogenated flame retardants will be banned in the future and there will be an increasing demand for halogen free flame retardants, especially zinc borate.

Zinc borates are multifunctional flame retardants primarily used as a polymer additive and preservative in wood composites. As a polymer additive, it serves as a fire retardant, smoke suppressant, afterglow suppressant and anti-arcing agent. In halogen free polymers, zinc borates promote char formation, reduce the rate of heat release, smoke evolution, carbon monoxide generation and afterglow combustion [2]. As 3 mol hydrated zinc borate retains its water of hydration at temperatures as high as 290-300 °C, it can be used in polymers and rubbers requiring high processing temperatures. Zinc borate can either be used alone, or more commonly, in synergistic reaction with other inorganic flame retardants, either halogenated or non-halogenated.

Zinc borates are synthetically produced borates from boric acid and zinc compounds. The general composition is $x\mathrm{ZnO}{\cdot}y\mathrm{B_2O_3}{\cdot}z\mathrm{H_2O}$, with $2\mathrm{ZnO}{\cdot}3\mathrm{B_2O_3}{\cdot}3\mathrm{H_2O}$ or $2\mathrm{ZnO}{\cdot}3\mathrm{B_2O_3}{\cdot}3.5\mathrm{H_2O}$ the most widely-used grade. In a study done by Schubert *et al.* [3], the structural characterization of zinc borate, $\mathrm{Zn[B_3O_4(OH)_3]}$, was investigated and it was found that the composition, $2\mathrm{ZnO}{\cdot}3\mathrm{B_2O_3}{\cdot}3.5\mathrm{H_2O}$, used in technical and trade literature, was $2\mathrm{ZnO}{\cdot}3\mathrm{B_2O_3}{\cdot}3\mathrm{H_2O}$ when analyzed by single crystal X-ray structural determination. So, it is appropriate to use $2\mathrm{ZnO}{\cdot}3\mathrm{B_2O_3}{\cdot}3\mathrm{H_2O}$ instead of $2\mathrm{ZnO}{\cdot}3\mathrm{B_2O_3}{\cdot}3.5\mathrm{H_2O}$.The synthesis of 3 (or 3.5) mol hydrated zinc borate was investigated in the previous studies [4-9] describing the effect of important reaction parameters. The synthesis was done via the heterogeneous reaction of boric acid and zinc oxide, Eq.(1):

$$6\mathrm{B(OH)_3(aq)} + 2\mathrm{ZnO(s)} \rightarrow$$

$$\rightarrow 2\mathrm{ZnO}{\cdot}3\mathrm{B_2O_3}{\cdot}3\mathrm{H_2O(s)} + 6\mathrm{H_2O(l)} \quad (1)$$

In mixing applications, scale up is indeed concerned with increasing linear dimensions from the laboratory to the plant size. In moving from laboratory to production scale, it is sometimes essential to have an

Correspondence: Institute of Nuclear Sciences, Ankara University, Tandogan, Turkey.
E-mail: gcakal@ankara.edu.tr; gayecakal@hotmail.com
Paper received: 24 Februry, 2012
Paper revised: 1 April, 2012
Paper accepted: 8 April, 2012

intermediate batch scale, so called the pilot scale. The process parameters determined at the laboratory scale are optimized at the pilot scale, and raw materials need not be consumed with the trials at industrial scale. However, inserting an intermediate scale between laboratory and production scale does not guarantee a smooth transition. Scale up of multiphase reactors, like zinc borate crystallization reactor, is quite cumbersome and very difficult. If the exact conditions such as crystallization medium, seed specifications and amount, and the process parameters such as temperature, stirring rate, reactants ratio, and process time, are not set properly, different crystals of zinc borate might be obtained. This is, of course, unwanted for an industrial scale production.

Up to now, all the studies concerning with the synthesis of zinc borate were performed either in laboratory [4–9] or pilot scale [8]. This is the first study in literature dealing with the production of zinc borate in industrial scale. Herein, the production of zinc borate, $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, is reported at the optimum reaction parameters by further increasing the pilot scale batch reactor capacity (85 L) to the industrial scale (1000 L). The samples taken in time intervals were analyzed to see the time dependent formation of zinc borate at this scale. The final product was also characterized. The reaction rate and the reaction completion time were compared with the small scale reactors. The reaction model adapted to the production of 3 mol hydrated zinc borate in the previous studies [4,8] was applied to industrial scale production by adding a lag time to the logistic model.

EXPERIMENTAL

Boric acid (H_3BO_3, with a purity of 99.9% by weight), zinc oxide (ZnO, with a purity of 99.9%), zinc borate ($2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$) and process water were used to produce zinc borate. Boric acid (H_3BO_3) was provided from Eti Mine Works, Emet Boric Acid Plant, Kütahya, Turkey. Zinc oxide with average particle size 0.95 μm (determined by laser diffraction analysis) was purchased from Metal Oksit Limited (İstanbul, Turkey). Zinc borate with the simplest formula of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ in size of 9 μm was purchased from U.S. Borax.

The industrial scale batch reactor used was a stainless steel reactor, volume of 1000 L, with a mechanical stirrer, heating jacket, thermocouple, and temperature control unit. The experimental procedure, analysis of boric acid and zinc oxide amounts in the solid samples, and particle size distribution by dry dispersion method were described previously [4].The industrial scale experiment was performed at 85 °C, at stirring speed of 170 rpm. The initial reactant (H_3BO_3/ZnO) mol ratio was 5:1. The zinc borate crystals initially added as seed were1.5 wt.% of the boric acid used.

TG/DTA Analysis of the final product was performed by a Perkin Elmer Pyris 1. The measurements were performed under N_2 flow of 100 mL/min. Uniform heating rate of 10 °C/min was applied during the measurements. To study the crystal structure of the produced zinc borate, powder X-ray diffraction analysis was carried out. XRD Patterns were recorded from 5° < 2θ < 50° by using a Rigaku D/Max 2200 PC X-ray diffractometer equipped with $CuK\alpha_1$ radiation. Images of the final products were obtained by scanning electron microscopy using a Carl Zeiss Supra 55 VP SEM instrument.

RESULTS AND DISCUSSION

The reaction of zinc oxide and boric acid was performed in industrial scale batch reactor by scaling up the laboratory and pilot scale batch reactors described in the previous studies [4,8]. The production of zinc borate in industrial scale is compared with the 4 L laboratory scale (run 6) and 85 L pilot scale reactor (run 11) experiments of the previous study [8], in which the operating conditions were the same as the industrial one. In scaling up the reactor, the stirring speed is adjusted by using the relationship [10]:

$$\frac{N_1}{N_2} = \left(\frac{D_2}{D_1}\right)^x \tag{2}$$

where N is the stirring speed (rpm) and D is the diameter of the stirrer. The exponent x was taken to be 0.667 with the assumption of homogeneous suspension of the solids.

In this study, the reaction temperature, initial reactants ratio, stirring speed, zinc oxide particle size and purity, and seed amount was kept constant by varying the reactor size to investigate the effects of scale up on the final product specifications, including the particle size, reaction time and conversion of zinc oxide to zinc borate. The kinetic model developed for the reaction in small scale reactor [4,8] was also adapted to the scale up production by using the data collected during the industrial scale reactor experiment.

Industrial scale product specification

The reaction between zinc oxide and boric acid was performed under the specified experimental conditions in the industrial scale reactor. The product obtained from the reaction was analyzed for its ZnO and B_2O_3 contents, dehydration temperature and particle

size. The results were listed together with the values of the commercial zinc borate and the zinc borates obtained from the previous study [8] in Table 1. The chemical analysis of the industrial scale product showed that the produced zinc borate has the ZnO, B_2O_3 and water percentages that of the commercial zinc borate. The water content of the product was also confirmed from the TGA analysis. As seen from Table 1, there were differences in the ZnO and B_2O_3 percentages of the zinc borates obtained in different scales. These differences were not quite significant as it did not change the XRD patterns of the final products [8] and also the properties of obtained zinc borates (Table 1).

To check the formation of produced zinc borate, XRD analysis was performed. The time dependent changes in XRD patterns of solid samples during the reaction between zinc oxide and boric acid in the industrial scale experiment are depicted in Figures 1 and 2 along with that of commercial $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ for comparison. It is clear from the figures that the formation of zinc borate did not begin until 210 min of the reaction and complete conversion was observed at 240 min. Scaling the reactor up to either 4, 85 or 1000 L did not change the XRD pattern of the 3 mol hydrated zinc borate products [8], which were also identical to the commercial zinc borate.

The results obtained from XRD powder patterns were confirmed by the SEM images given in Figure 3. In industrial scale production, no zinc borate crystal was observed within the first 150 min, as seen from the SEM image in Figure 3b. This image is identical to the one in Figure 3a, in which only ZnO powder having particle size of ≤1 μm exists. As proposed in the previous studies [4,8], the reaction of zinc borate production proceeds on the surface of the ZnO particles, which was also observed from Figures 3c-3f. As seen, zinc borate grains consisting of irregular platelets were formed. In industrial scale reactor, zinc borate production did not begin until 210 min of the reaction (Figure 3c), which is in accord with the XRD results. On the other hand, zinc borate produced at the laboratory scale (run 6 of the previous study) did not form until140 min of the reaction [8].

It is observed form Figure 4 that during the industrial scale synthesis of zinc borate, there is a time lag of 120 min. The initiation of the reaction delays because of the reactor volume as mass transfer effect

Table 1. Final product specifications and logistic model parameters for the laboratory, pilot and industrial scale zinc borate production

Scale	Final product specifications				Logistic model parameters		
	ZnO %	B_2O_3 %	Dehydration temperature, °C	Average particle size, μm	Specific growth rate k / min^{-1}	Normalized critical initial concentration, χ_0	R^2
Seed[a]	37.5	48.0	290	8.8[b]	-	-	-
Lab	39.9	45.7	340	3.8	0.054	0.0014	0.898
Pilot	38.2	48.7	330	3.4	0.044	0.0095	0.983
Industrial	38.1	46.6	340	4.3	0.050	0.0225	0.960

[a]US Borax Firebrake ZB, http://www.boraxfr.com/productsmain-1.html; [b]reported as 9 μm

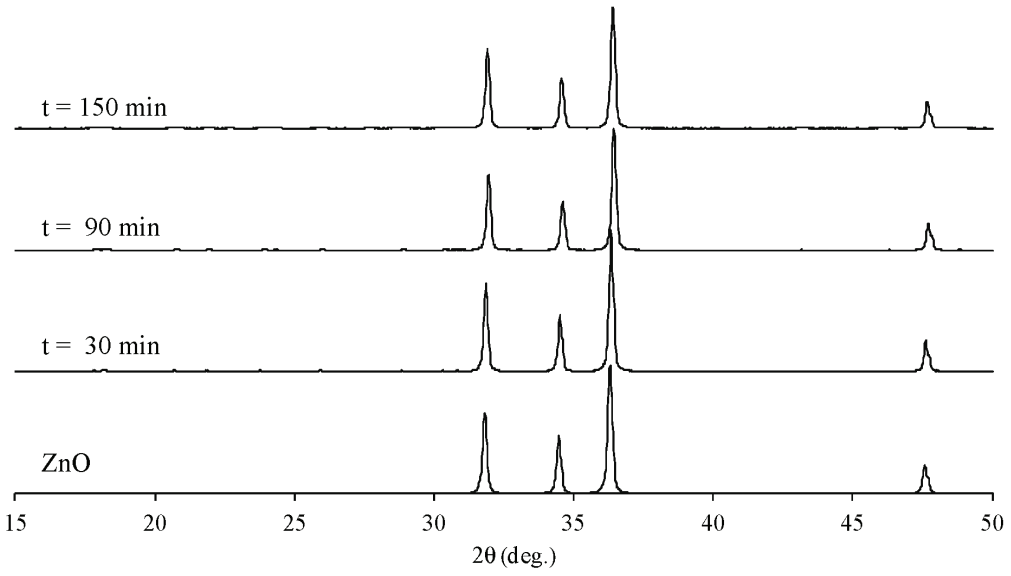

Figure 1. XRD Powder patterns of ZnO, solid samples taken from the industrial scale experiment with respect to time (0-150 min).

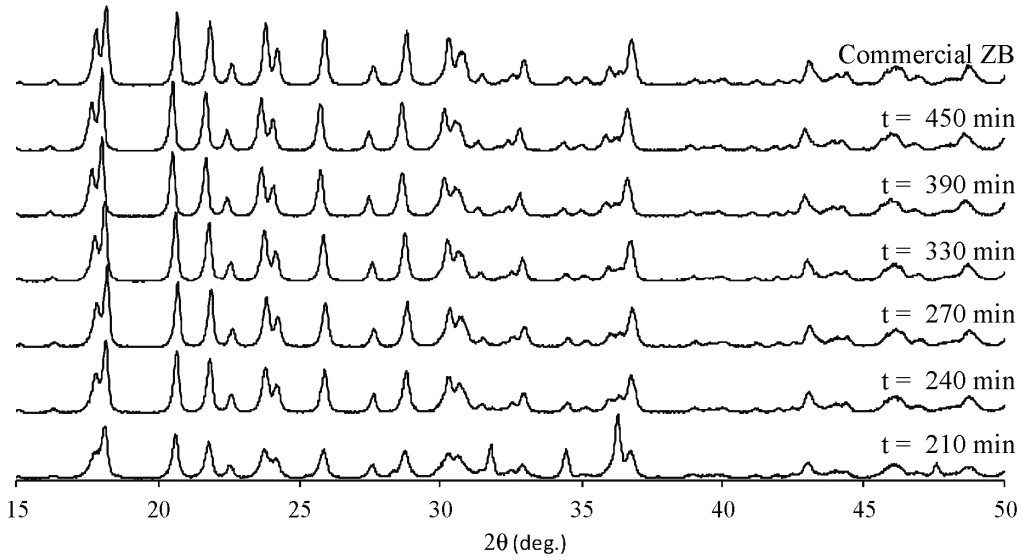

Figure 2. XRD Powder patterns of solid samples taken from the industrial scale experiment with respect to time (210-450 min) and commercial zinc borate Firebrake ZB.

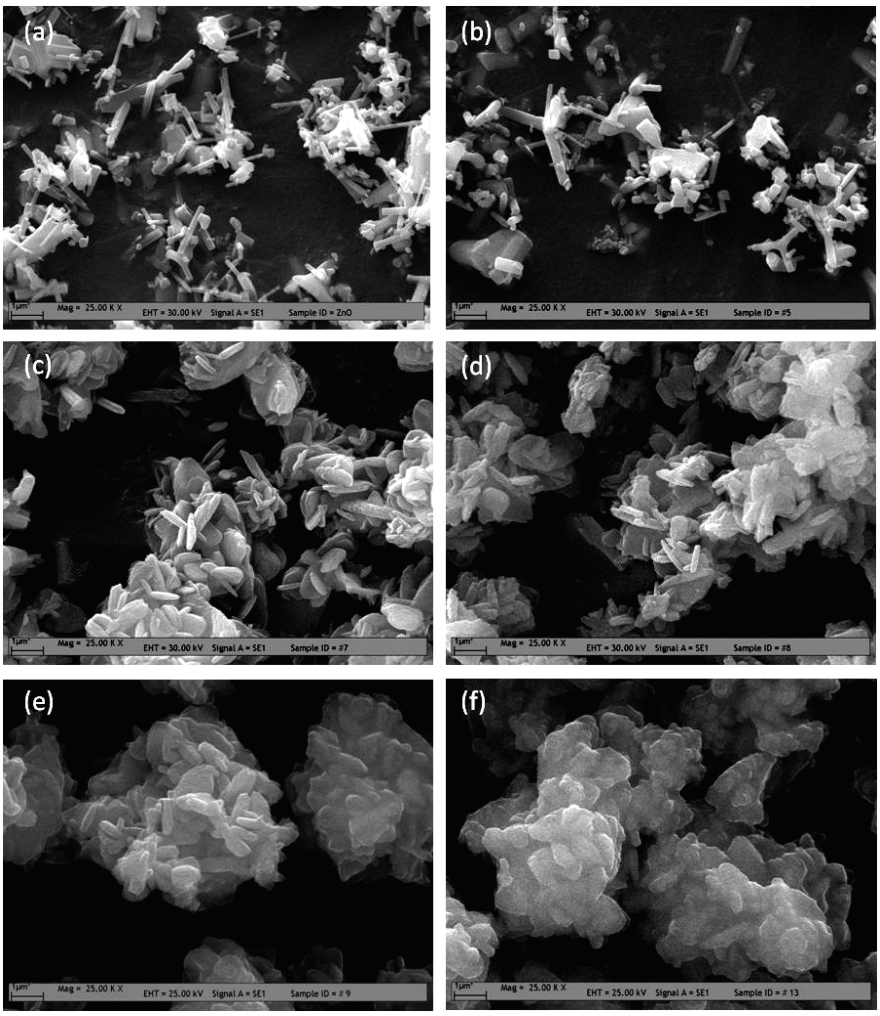

Figure 3. SEM Micrographs of industrial scale reactor experiment, a) 0, b) 150, c) 210, d) 240, e) 270 and f) 390 min after reaction initiates (temperature 85 °C, seed amount 1.5%, initial reactants mole ratio (H_3BO_3:ZnO ratio of 5:1), stirring speed 170 rpm, and average particle size of zinc oxide particles 0.95 μm).

takes place during this time in industrial scale. The reaction completion time in industrial scale experiment is 240 min whereas this time is shorter for pilot and laboratory scale experiments. From the comparison of time dependent XRD patterns, SEM images and chemical analysis for laboratory and industrial scale reactor experiments, a 70 min time difference was found for the reactions to complete. When the time lag of 120 min in industrial scale is taken into account, this time difference seems quite reasonable.

Although zinc borate crystals are in the shape of agglomerates, the laser diffraction analysis gives an average particle size of 4.3 μm (Table 1). In order to confirm the constant particle size after complete conversion, the samples at 240 and 450 min are analyzed with laser diffraction particle size analyzer. It was found that the particle size did not change with time after complete conversion. Besides, the scaling up the reactor to industrial one did not have a significant effect on the particle size. The laboratory scale and pilot scale product particle sizes were found as 3.8 and 3.4 μm, respectively [8] (Table 1). As zinc borate is used as a flame retardant additive, particularly in polymers, particle size is of great importance to its industrial applications. For example, in wire and cable applications, finer particle sizes of flame retardant additives are utilized for higher limiting oxygen index (LOI) values, improved mechanical properties, lower brittleness temperatures, and smoother surface characteristics [11].

The hydration water of the 3 mole of hydrated zinc borate was determined in the previous studies [4,8], as zinc borate is widely used as a flame retardant additive in plastics and it is important that zinc borate releases its hydration water above the processing temperature of the plastics in order to preserve its effect. TGA Results showed that the zinc borate product, $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, obtained from laboratory, pilot and industrial scale reactor experiments, has a dehydration temperature higher than that of the commercial one (Table 1). The dehydration starts at 330–340 °C. The initial weight loss during the dehydration corresponds to the removal of 3 moles of H_2O per formula of zinc borate product as expected [12].

Conversion of zinc oxide in industrial scale

The formation of zinc borate is a heterogeneous reaction taking place in aqueous medium, as the zinc oxide is insoluble in water and boric acid is soluble in water at the reaction temperature, Eq. (1).The crystal growth of zinc borate from the reaction of zinc oxide and boric acid was interpreted by using the logistic model. The effect of the operating conditions on the parameters of the logistic model was studied [4,8]. In what follows, the effect of scale up on the specific growth rate obtained at different reactor volumes are discussed.

The extent of reaction in zinc borate crystallization is given by conversion of ZnO to zinc borate. Data for the conversion of zinc oxide versus time was fit to the logistic model as given by the following rate equation [4]:

$$\text{Rate} = \frac{\mathrm{d}X}{\mathrm{d}t} = k\left(1-\frac{X}{X^*}\right)X \tag{3}$$

where the rate of crystal growth for zinc borate in M/min is equal to $\mathrm{d}X/\mathrm{d}t$ in the case of batch reactor, X is the zinc borate concentration (M) in the slurry reactor, $X^*$is the maximum zinc borate concentration (M), k is the specific growth rate (1/min). When X is equal to X^*,the crystal growth rate is zero.

In industrial scale production of zinc borate, a 120 min time lag was observed (Figure 4), which should be taken into account during modeling. So, by inserting the lag time, t_{lag}, in Eq.(3) and integrating, the rate law becomes:

$$X = \frac{X^*}{1+\left(\frac{X^*}{X_o}-1\right)\mathrm{e}^{-k\,(t-t_{\text{lag}})}} \tag{4}$$

where X_o is the critical initial concentration of zinc borate. Using the normalized concentrations ($\chi = X/X^*$ and $\chi_o = X_o/X^*$) will reduce the number of parameters to two, k and χ_o in the integrated form of rate equation:

$$\chi = \frac{1}{1+\left(\frac{1}{\chi_o}-1\right)\mathrm{e}^{-k\,(t-t_{\text{lag}})}} \tag{5}$$

This equation can be rearranged into linear form:

$$\ln\left(\frac{1}{\chi}-1\right) = -k(t-t_{\text{lag}}) + \ln\left(\frac{1}{\chi_o}-1\right) \tag{6}$$

Either using the curve fitting software, Microsoft Excel, the experimental data were fit to the integrated rate law, Eq. (4) or the linear regression of the data with Eq. (6), the values of two model parameters k and χ_o were obtained and listed in Table 1. It is worth to mention that the normalized concentration is the conversion of zinc oxide since the X^* is the maximum concentration of zinc borate at complete conversion. X_o values are related to the seed concentration, added to the solution at the beginning of reaction.

The industrial scale experimental data is fitted to the modified logistic model with time lag and represented in Figure 4 together with the laboratory and pilot scale experiments [8]. The parameters found

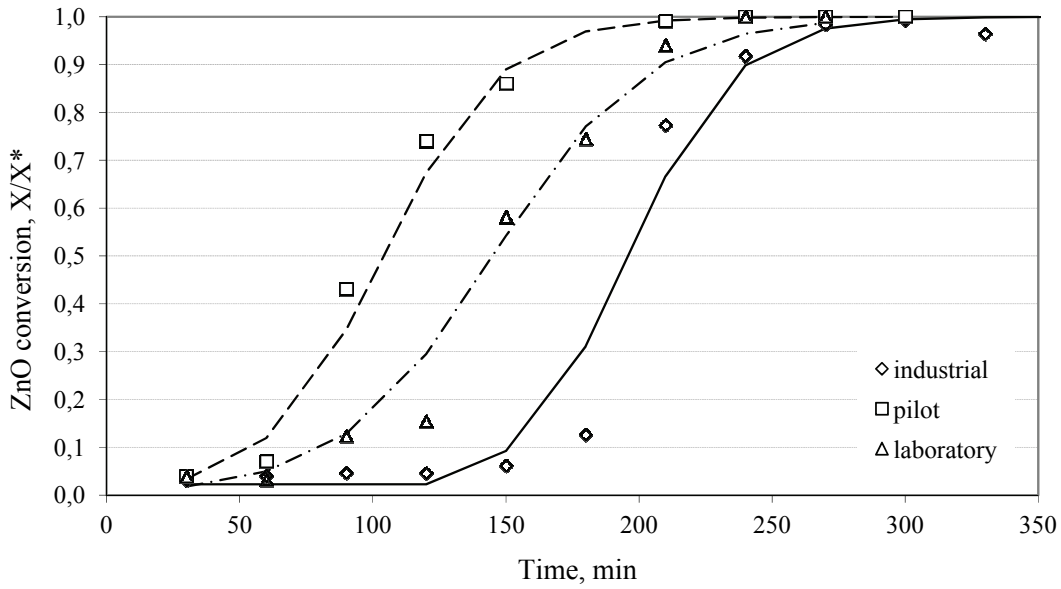

Figure 4. ZnO Conversion vs. time graph of the experiments to observe the effect of scale-up (temperature 85 °C, seed amount 1.5%, initial reactants ratio (H_3BO_3:ZnO ratio of 5:1), and average particle size of zinc oxide particles of <1 μm were constant). Curves denote the logistic model.

from the logistic model are presented in Table 1. As seen, the specific growth rate, k, did not vary much with the increase in reactor volume, whereas the critical initial concentration, χ_o, increased considerably with reactor volume. As the specific growth rate is a way of measuring how fast the zinc borate crystals are produced, it is an important finding to obtain the specific growth rates being independent of the reactor volume. The increase in the critical initial concentration with scale up refers to increase of the zinc borate added to the solution as seed at the beginning of the reaction with the increase in reactor volume. As mass transfer effects take place at the beginning of the reaction (lag time) in industrial scale, this result seems quite reasonable. With an increase in the seed amount, the concentration of zinc borate will increase, which will shorten the lag time.

CONCLUSIONS

$2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ was successfully produced at industrial scale *via* solid-liquid reaction of boric acid and zinc oxide. It has been observed that zinc borate crystals have an average particle size of 4.3 μm and hydration temperature of 340 °C. The final product has the same specifications as that of the products obtained at laboratory and pilot scales, which is very promising for commercialization. This result strongly implies that the critical scale-up parameters are well specified (temperature, stirring speed, etc.) even for this complex multiphase crystallization reaction.

The model proposed for the crystallization rate in the previous studies [4,8] was verified at the industrial scale with a modification that includes slag time. A good fit of the experimental data to the logistic model was obtained. The model parameter, specific growth rate, k, remained unaffected by scaling up showing that the crystal growth rate is independent of the hydrodynamics of the reactor. Finally, the increase of the model parameter, normalized critical initial concentration, χ_o, with reactor volume shows that the seed concentration has to be adjusted properly if the reactor volume is increased to industrial scale. As there is a lag time at the beginning of the reaction in industrial scale, this time lag can be set near to zero with the adjusted seed amount.

Acknowledgements

Support of this work by National Boron Research Institute (BOREN) is gratefully acknowledged. The author is grateful to BMBT Büyükmıhçı Boron Technologies R&D, Inc., Kayseri, Turkey, for the industrial scale production, Eti Mine Works, for the supply of boric acid, Geological Engineering Department of Hacettepe University and Central Laboratory of Middle East Technical University for the analyses.

REFERENCES

[1] Roskill Information Services Ltd., Boron: Global Industry Markets and Outlook.12th ed., London; 2010

[2] K.K. Shen, S.H. Kochesfahani, F. Jouffret, in: Fire Retardancy of Polymeric Materials, C.A. Wilkie, A.B. Morgan

Eds., CRC Press, Taylor & Francis Group, New York, 2010, p. 207

[3] D.M. Schubert, F. Alam, M.Z. Visi, C.B. Knobler, Chem. Mater. **15** (2003) 866-871

[4] D. Gürhan, G.Ö. Çakal, İ. Eroğlu, S. Özkar, J. Cryst. Growth **311** (2009) 1545-1552

[5] A.V. Shete, S.B. Sawant, V.G. Pangarkar, J. Chem. Tech. Biotechnol. **79** (2004) 526-532

[6] H.E. Eltepe, D. Balköse, S. Ülkü, Ind. Eng. Chem. Res. **46**(8) (2007) 2367-2371

[7] D. Gürhan, G.Ö. Çakal, İ. Eroğlu, S. Özkar, TR Patent 02072 B (2006)

[8] M. Kılınç, G.Ö. Çakal, S. Yeşil, G. Bayram, İ. Eroğlu, S. Özkar, J Cryst. Growth **312** (2010) 3361-3366

[9] X. Shi, Y. Xiao, M. Li, L. Yuan, J. Sun, Powder Technol. **186** (2008) 263-266

[10] F. Aerstin, G. Street, Applied Chemical Process Design, Plenum Press, New York, 1978

[11] J.M. Cogen, T.S. Lin, P.D. Whaley, in: Fire Retardancy of Polymeric Materials, C.A Wilkie, A.B. Morgan Eds., CRC Press, Taylor & Francis Group, New York, 2010, p. 783

[12] D. Gürhan, M.Sc. Thesis, Middle East Technical University, Ankara, 2005.

GAYE Ö. ÇAKAL

National Boron Research Institute, BOREN, Ankara, Turkey

NAUČNI RAD

INDUSTRIJSKA PROIZVODNJA FINOG CINK-BORATA

U ovom radu je izvršena proizvodnja cink-borata u industrijskom šaržnom reaktoru pri optimalnim procesnim uslovima utvrđenim u prethodnim studijama izvršenih u laboratorijskom i poluindustrijskom reaktoru. Proizvodnja je izvršena heterogenom reakcijom borne kiseline i cink-oksida. Uzorci su okarakterisani hemijskom analizom, XRD, TGA, SEM i distribucijom veličine čestica. Finalni proizvod dobijen u industrijskom reaktoru je formule $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$. Kinetički podaci za produkciju cink-borata se poklapaju sa modifikovanim logističkim modelom, gde se vreme kašnjenja uzima u obzir. Zapaženo je da reakcija zavisi od razmere procesa. Vreme kašnjenja u industrijskim razmerama je bilo 120 min i reakcija je trajala 70 min duže od reakcije u poluindustrijskom reaktoru. Treba naglasiti da specifična brzina reakcije, k, kao i prosečna veličina čestica i temperature hidratacije cink-borata, ne zavise od veličine reaktora.

Ključne reči: cink-borat; povećanje razmere; industrijska proizvodnja; kinetika; logistički model; kristaliti.