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Crystallization kinetics of Sodium Sulfate Decahydrate in an MSMPR stirred crystallizer

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Experimental work on a sodium sulfate-water system was carried out using two liter crystallizers by cooling. Different impeller velocities and suspension densities were used. Experimental evidence from continuous crystallizers frequently shows, at least for small crystals, deviation from the McCabe ΔL law. The relation between growth rate and particle size is investigated. The methods of estimation of kinetics for industrial use are discussed. The experimental data of population density distribution was fitted directly by the three-parameter model presented by Mydlarz and Jones for a steady state MSMPR crystallizer. The relationship between the parameters of kinetics of both nucleation and growth rate and supersaturation was obtained by analyzing experimental data.

1. Preface

The simulation, design and control of bulk suspension crystallizers depend on the accurate prediction of the crystal size distribution (CSD). It is well known that the CSD is dependent on the nucleation and growth kinetics and residence time distribution within the crystallizer and can be predicted using population balance techniques (Randolph and Larson, 1971). Crystallization kinetics are commonly measured using the continuous mixed suspension mixed product removal (MSMPR) crystallizer technique, which permits simultaneous determination of both growth and nucleation rates by analysis of the CSD at a given mean residence time. The measured kinetic data can then be correlated with appropriate growth and nucleation rate models. Experimental evidence from continuous crystallizers shows, at least for small crystals, deviation from the McCabe ΔL law in a number of systems. The estimation of kinetics of both nucleation and growth rate becomes more complicated. The crystal growth dispersion, nucleation dispersion and crystal size-dependent growth, as well as the retention time distribution and classification all result in the deviation from the McCabe ΔL law law. For mechanism studies, observation of crystal behavior in the subsieve range has been done by many workers (Garside et al, 1976; Ulrich et al 1991; Garside et al, 1979; Wang et al, 1990). It was found that each crystal can grow at a different, constant rate, while some of crystals neither grow nor dissolve. On the other hand the crystal size distribution obtained in a continuous crystallizer is the result of all these phenomena. The "apparent" growth rate and nucleation rate is the combination of the

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above phenomena. It is still not very clear how information from the small crystal can be used in the estimation of crystallization kinetics in the MSMPR crystallizer.
The crystallization kinetics of sodium sulfate decahydrate from aqueous solution were investigated in this work. The experimental work has been done in a 2 liter continuous MSMPR cooling crystallizers. The suspension density and temperature were changed so that the influence of operational conditions on crystallization kinetics can be revealed. The crystal size distribution was determined over the range of the crystal sizes from 0.04um to the largest crystals, which have been produced in the crystallizers by Beckman LS 13 320 light scattering laser analyzer. The relation between growth rate and particle size was discussed, especially for small crystal sizes. The model of nucleation and growth rate were developed based on experimental data.

2. Experiment procedure

The experimental apparatus and procedure were described in the Fig. 1. The crystallizers are cylindrical stainless steel vessels. Agitation is provided by a four-blade pitch-type impeller, located in the center of crystallizer. The feed solution is introduced into the middle of the crystallizer just above the impeller. The product crystals were removed by a pump through a 8 mm plastic pipe. The product removal pump was continuous in operation. The liquid level was controlled by ultrasonic liquid level meter, which conducted the signal to two valves which determined the suction rate from the crystallizer.

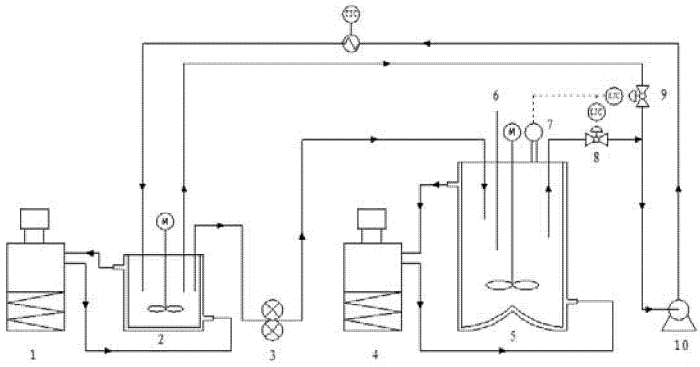

Fig. 1 Schematic diagram of experimental apparatus 1,4 cooling equipment, 2 feed tank ,3 feed pump, 5 crystallizer, 6 thermometer, 7 ultrasonic liquid level meter, 8,9 electric valve, 10 product remove pump.

All experiments were carried out at set temperatures, feed rates and impeller rotation speeds. Supersaturation was produced by cooling. The crystallizers were normally operated for at least eight residence times to ensure the steady state was attained. At the end of each experiment crystal samples was taken from crystallizer and analyzed by Coulter LS 13 320 Laser scattering. As the same time, sodium sulfate concentration in mother liquor was analyzed by chemical analysis for calculation of the supersaturtaion.

3. Results

The population density was calculated from the measured mass distribution of crystals. A a typical run is shown in Fig.2. The plot ln[n(L)] versus L for all experiments presented a upward curvature, which means a size-dependent growth rate. Several models can be used for estimation of the crystallization kinetics for the case of size dependent crystal growth. The model presented by Mydlarz and Jones (1989) was selected in this work.

$$G(L) = G_{\max}\{1 - \exp[-a(L + c)]\} \quad (1)$$

According to this size dependent growth rate model, the population density distribution can be estimated with the following equation as given by Mydlarz and Jones.

$$n(L) = n^0 \exp(aL)\left[\frac{\exp(ac) - 1}{\exp(ac)\exp(aL) - 1}\right]^{(1 + a\tau G_m)/a\tau G_m} \quad (2)$$

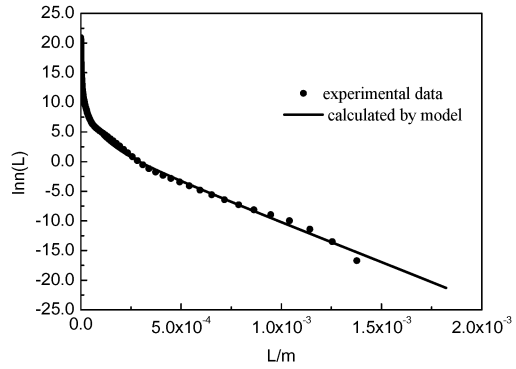

Fig. 2 MSMPR crystallization of sodium sulfate decahydrate. Population density for a typical run.

In order to obtain the size dependent crystal growth rate model, the parameters in the growth rate model for each operation condition have to be estimated, which corresponding a certain supersaturation of the crystallization process. Further, the model of crystal growth rate with depebdebt of supersaturation can be established.
The parameters in the crystal growth rate model were estimated by fitting the measured population density distribution with the Eq. (2). The relation between growth rate and particle sizes for a typical run is shown in Fig. 3. It clearly shows that the large size of crystals have large vules of the crystal growth rate.

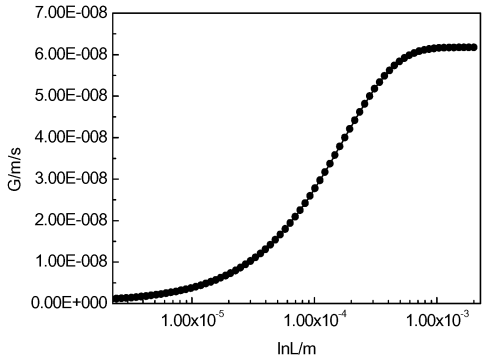

Fig. 3 The relation between growth rate and crystal size on the logarithmic scale of the crystal size L

The parameters G_m, a, and c in the growth rate were correlated to the supersaturation with the following eautions.

$$G_{\mathrm{m}} = 1.16\times10^{-8} + 9.81\times10^{-9}\exp(0.67\times\Delta C) \quad (3)$$

$$a = 2.54\times10^{4} - 2.53\times10^{4}\exp(-0.19\times\Delta C) \quad (4)$$

$$c = 3.03\times10^{-7} + 2.51\times10^{-6}\exp(-1.24\times\Delta C) \quad (5)$$

The experimental relationships between the parameter G_m, a, c and supersaturation were shown in Figs. 4, to 6. Average deviation of the models given for Gm, a and c with the experimental results is 18.2%, 21.5% and 19.4%, respectively

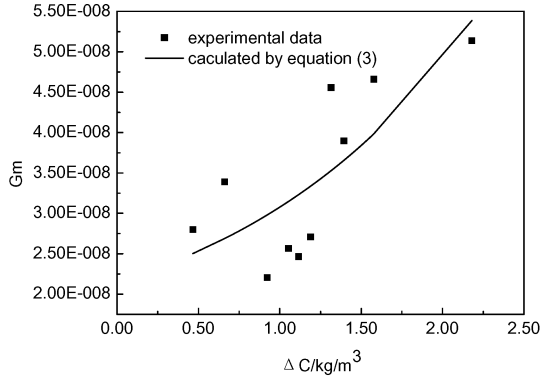

Fig. 4 The relation between the parameter Gm and supersaturation

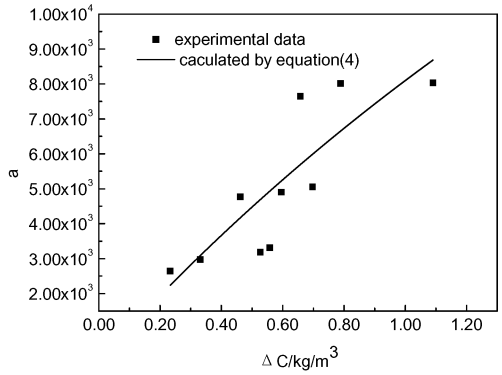

Fig. 5 The relation between the parameter a and supersaturation

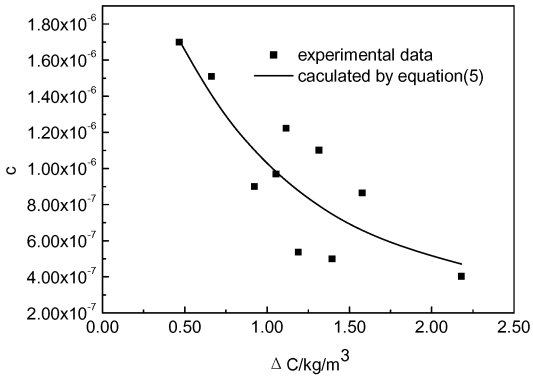

Fig. 6 The relation between the parameter c and supersaturation

For estimation the nucleation rate, the zero size of the nuclei was general used. However, for the size dependent crystal growth system, the nucleation rate at zero size is hard to be estimated well. The effective nucleation rate was estimated based on the method proposed by Sha et al. (1996). As can be seen from Fig. 3, when the crystal size is smaller than 0.4um, the crystal growth rate is not changed much. Therefore, the nucleation rate was calculated based on the crystal size of 0.4 um. Therefore, the nucleation rate was calculated by the population density at crystal size of 0.4um multiplied by the growth rate at the crystal size of 0.4um.

$$B^* = B_{0.4} = n_{0.4} G_{0.4} \quad (6)$$

Several parameters affect the nucleation rate shuch as the supersaturation, suspension density, mixing intensity and temperature. The general nucleation rate could be given as.

$$B^* = K\exp(-E^*/RT)\Delta c^i M_T^j N^n \quad (7)$$

Based on the operation conditions and the parameter values of the experimental data, the nucleation rate can be fitted with the general model with the relative parameters as follows with average deviation of 26.1%:

$$B^* = 2.73\times10^{-5}\exp(-0.34/RT)\Delta c^{1.01} M_T^{1.99} N^{0.23} \quad (8)$$

The results shows that supersaturation is main factor which determine rate of the crystal growth. The three parameter model may imitate the crystal size-dependent growth system, in which each parameter is related with supersaturation. The values of parameter Gm and a increase with increasing supersaturation Δc in the crystallizer. It indicates maximal crystal growth rate is positive pertinence to supersaturation. While the values of parameter c which maybe have great pertinence to critical growth size of crystal decrease with increasing supersaturation Δc in the crystallization system. It is logical "effective" zero-size gets less when supersaturation Δc in the crystallizer increase.

4. Conclusions

The growth of sodium sulfate decahydrate crystals is size-dependent. The relationship between the parameters in the crystal growth model and supersaturation was established for the system studied. The effective nucleation rate defined at crystal size of 0.4 um was modlled with superstation, mixing intensity, suspension density and temperature. The models can be sued in the crystallization process design and control.

References

Randolph A.D. and Larson M.A., 1971, Theory of Particulate Processes. Academic Press, New York.

Garside, John, Jancic, Slobodan J., 1976, Growth and dissolution of potash alum crystals in the subsieve size range, AIChE Journal, v 22, n 5, 887-894

Ulrich J., Kruse M., Kallies B. and Garside J., 1991, Growth rates of potassium sulphate crystals of different surface qualities in the size range from 10-100μm, Chem Eng Commun , v 99, n 1, 25-32.

Garside J., Rusli I.T. and Larson M.A.,1979, Measurement and scale-up of secondary nucleation kinetics for the potash alum-water system, AIChE Journal, v25, n6, 948-958.

Wang S., Mersmann A. and Kind M., 1990, Verification of the constant crystal growth model for attrition particles and its relevance to the modelling of crystallizers, Crystal J., Growth 99, 1104.

Mydlarz J. and Jones A.G.,1989, On modelling the size-dependent growth rate of potassium sulphate in an MSMPR crystallizer, Chem Eng Commun , 90, 47.

Sha Z L, Hatakka H, Louhi-Kultanen M, Palosaari S.,1996, Crystallization kinetics of potassium sulfate in an MSMPR stirred crystallizer, Journal of Crystal Growth, v 166, n1-4, 1105-1110.