NUCLEATION KINETICS OF AMMONIUM PERCHLORATE

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ABSTRACT

Metastable zones and nucleation kinetics of ammonium perchlorate in a magnetic stirrer have been determined for both seeded and unseeded solutions by measuring the maximum allowable undercooling temperature. The determination was commenced through temperature range between 30 and 60 °C. This range had been subjected to different rates of cooling that range between 0.5 and 2 °C/min.

It was found that the width of metastable zone had increased with cooling rate. Furthermore, lower nucleation rate of ammonium perchlorate for the unseeded solution than for the seeded solution was found. Eventually, the metastable limits for ammonium perchlorate have relatively narrow limits e.g., between 2.00 to 3.60 °C for the unseeded solution and between 1.20 to 2.65 for the seeded solution.

To study the effects of the rate of cooling and the isothermal duration time on crystal size distribution, the experiments are carried out in a batch crystallizer by cooling an aqueous solution where the cooling rate is maintained at a specified rate to keep the temperature decrease at a linear pattern. The presented data shows that lower rate of cooling produce greater median size than higher rates. While, isothermal duration time had shown less size dependence, long isothermal duration time affected the size of the produced crystals as smaller median sizes had found.

INTRODUCTION

Crystallization is one of the basic processes in the final treatment of the products in the chemical industry. In spite of the fact that the number papers on crystallization is rapidly increasing, it is not possible to state that the problems involved in this operation are unambiguously solved. Kinetic data on crystallization process are of basic importance for the design of industrial crystallization equipment. These data determine the size of the crystallizer and the crystal size of the product, and consequently even-increasing attention is being rapid in the literature to the kinetics of crystallization (Nývit, 1989).

The crystallization process consists of two stages. The first, called nucleation, which is the formation of the solid phase, whereas the second, entitled growth, which is the build-up of layer • of solute on the nucleus (Ullman, 1988). Supersaturation is the driving force for both stage of the process. The degree of the supersaturation or deviation from equilibrium of saturated condition is the main factor controlling the deposition process. The supersaturation of a system may be achieved by cooling, evaporation, or as a result of chemical reaction. In other words, the crystallization and nucleation phenomena occur where solute concentration exceeds solute solubility (William, 1994).

Formation of crystalline masses implies conjunction between nucleation and crystal growth. Nevertheless, due to the complexity of each one of these different stages, in order to perform studies, which establish clear conclusions about crystal growth, it is of great importance to control the system at maximum and avoid non-expected phenomena, i.e., primary or secondary nucleation during crystal growth experiments (Grases, 1993).

Nucleation and crystal growth are represent by a rate equation of the following forms:

$$\frac{dm}{dt} = k_n \Delta C_{max}^{n} \qquad \text{for nucleation}$$

$$\frac{dm}{dt} = k_g A_s \Delta C^{g} \qquad \text{for crystal growth}$$

The present study is mainly directed to study the kinetics of crystal growth and nucleation for ammonium perchlorate and state the expression rates for nucleation in according to the previous mentioned form. Although, the process has a great complexity and distinction between the two mechanism that conducted through crystal formation take a great deal of attention. Therefore, the experimental study that conducted during the kinetic study of nucleation rate would take another category from that followed through the study of crystal growth rate of ammonium perchlorate conducted in previous work of the authors (Nahidh *et al,* 2000).

Crystallization from solution is of enormous economic importance. Many products of the chemical industry are purified by crystallization, often in vast tonnage (Van Damme, 1973). In general crystallization is usually occurred in two subsequent mechanism (i.e. nucleation and crystal growth mechanisms). Nucleation mechanism involves the assembly of solute molecules into specific concentrated array as a result of their normal molecular motion. The assembly may exist only momentarily, because, in addition to the attractive and repulsive forces between the molecule, there are the disruptive forces of solvent molecule movements and connective eddy currents acting on the entire system (Bruce, 1965). Simple visualization of nucleation currency is the formation of sufficient number of molecules into aggregates until the tendency for further growth is greater than the tendency to loss molecule. The number of molecules necessary to form this critical size apparently varies widely, depending on the compound and conditions, e.g. eight molecules have been estimated to be required for $BaS0_4$, which dose not imply that eight molecules of $BaS0_4$ have been collide simultaneously to form the critical nucleus, but rather that cluster of various sizes exit in the solution and that a stable collision only need occur with two clusters of total eight or more molecules (Donald, 1958).

Depending upon circumstances regarding the crystallization system and its environment, the nucleation mechanism may distinguish as shown in Fig (1).

Primary nucleation generally takes place in the absence of solute crystals or in the presence of solute crystals at conditions where these latter exert little or no influence. Primary nucleation may be distinguished as a homogeneous nucleation and heterogeneous nucleation (Nývit, 1989). Where the homogeneous nucleation occurs within a homogeneous solution as no foreign surface previously exists. The creation of solid particles within a homogeneous continuum demands a certain energy consumption to form a solid surface. On the other hand, molecules forming interior of a solid particle release a quantity of energy which corresponds to the restriction of the mobility of molecules. Therefore, the total quantity of work required to form a stable crystal nucleus is equal to the sum of the work required to form the surface and the work required forming the interior of the particle.

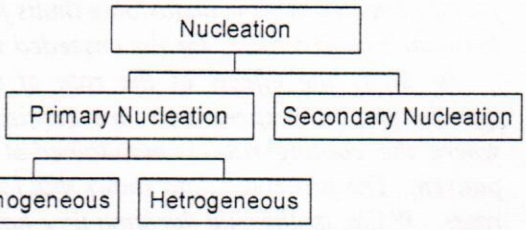


Fig. (1) Mechanisms of nucleation step (Janâc, 1984)

The overall excess free energy change associated with process of homogeneous nucleation is by analogy the difference between the surface excess free energy AGs and volume excess free energy AGv (Janac, 1984).

While, the heterogeneous nucleation usually occurred in the presence of the foreign surface. It thought that the influence of the foreign surface is catalytic, and that the activation energy for nucleation may thereby be reduced (Elwell, 1975). Eventually secondary nucleation requires the preexistence of parent crystals, which are involved in the initiation of further nucleation by three mechanisms:

1. Breakage.
2. Attrition due to collisions.
3. Removal of semi-ordered surface layers through fluid shear.

Ting and Macabe (1934) demonstrated that the solution nucleated in a more reproducible manner at moderate supersaturation in the presence of seed crystals. Power (1963) indicated that movement of the solution passed a stationary crystal produced nuclei. These results were tended to suggest that a fluid mechanical shearing of weak outgrowth or loosely bonded molecular unit from the crystal-solution interface was responsible. In another study, Melia and Moffitt (1964) noticed that the rate of secondary increased with supersaturation and agitation.

Undermost commercial operating conditions the three mechanisms of nucleation can be presumed to take place simultaneously. All the three mechanisms depend on the same principal variables: supersaturation, the concentration of the crystals in the slurry and the agitation conditions. These are described by single empirical relation (Power, 1963):

$$R_n = k_n \Delta C^n M_t^b N^m \exp\left(-\frac{E}{RT}\right) \qquad (1)$$

This process is manifested by the regular deposition of the excess solute from the solution on the various faces of a crystal. The result is a decrease in concentration of the solution and increase in a crystal size. The velocity at which the crystal face moves outward in a direction normal to the face may specify the rate of increase in crystal size. This velocity is called the linear face growth rate. Different faces of crystal may grow at different rates, and so the average linear growth rate if often approximated by the increase diameter of a sphere having the same volume as the crystal, or by the increase in a characteristic dimension of the crystal. The growth of crystal from solution is at least a three-stage process:

1. The transport of solute from the bulk of the solution to the vicinity of the crystal surface.
2. Some processes at the crystal surfaces, probably involving adsorption into the surface layer followed by the orientation of the molecules into the crystal lattice (often referred to as surface integration process).
3. Dissipation of the heat of crystallization liberated at the crystal surface (Janâc, 1984).

It is generally accepted that the first two processes are governed mainly by the concentration driving force.

Noyes and Whitney (1897) postulated that the rate of crystallization is determined only by the rate of diffusion to the crystal surface, where it was suggested the concentration is that of the saturated solution. However, Miers (1904) observed that the solution is contact with growing crystal face is supersaturated. Starting from this point Berthoud (1912) suggested that the process of diffusional transfer is followed by a first order reaction at the crystal solution interface.

As soon as the crystal nuclei are formed in saturated solution, they begin to grow. Their growth is specified by the linear crystallization rate which depends on the degree of supercooling, the relative velocity of the crystal with respect to the solution, the temperature, the characteristic of the crystal surface, and other parameters (Mullin, 1972). The kinetics of crystal growth of ammonium perchlorate had been extensively studied by the author in his previous study on ammonium perchlorate (Nahidh *et al*, 2000).

EXPERIMENTAL WORK

The estimation of the parameters of the nucleation kinetics expressions for seeded and unseeded solutions at different isothermal temperatures (30-60 °C), aqueous solution of ammonium perchlorate in a batch agitated vessel crystallizer had been subjected to different rates of cooling (0.5-2 °C/min). In addition, size distribution of the produce crystal from an aqueous solution of ammonium perchlorate, had studied in terms of different rates of cooling and different isothermal duration times.

By all means, in order to study the kinetics of nucleation of ammonium perchlorate (AP), the solubility curve of our own material by which the experimental work had conducted, must accurately determined. This was ascertained to avoid an appreciable error that might result from the inconsistency, which was found in solubility data between the material of our concern with data found in literatures. This inconsistency between the measured solubility data with the published data has arisen if impurities had encountered. Accordingly, solubility curve of our own material had determined throughout temperature range between 30 to 60 °C.

Apparatus

The determination of supersaturation curves and consequently the metastable limits was commenced in a 200 ml Erienmeyer flask fitted with a magnetic stirrer, and a digital temperature reader which incorporated with a calibrated thermocouple. A schematic diagram of the apparatus had been illustrated in Fig (2). The flask was immersed in a water bath. The temperature of the cooling medium (water) was carefully controlled via two needle valves suited at the inlet and exit ports to alter the flow rate of the inlet and outlet streams from the bath. A 100 W lamp was used for good observation to illuminate the sample under test.

Experimental procedure

100-ml of saturated solution of prescribed concentration had been prepared. Afterwards the solution had been introduced in a flask supplied with an enclosure to minimize evaporation of water that concurrent to a serious error. The enclosure was supplied with a calibrated thermocouple. Later on, the solution was heated to 10 °C higher than the prescribe temperature to ensure complete solvating of the stock. Afterward, the solution was cooled incrementally at constant rate till the desired temperature was reached. This was accomplished by adjusting the flow rate of the coolant medium (water).

At first sight of nucleus formation, the temperature of the solution was recorded. The difference between the saturation and nucleus formation temperature represents the maximum allowable undercooling difference (ΔTmax) that corresponds to the particular cooling rate. This maximum allowable undercooling difference may interpret latter to determine the maximum supersaturation allowance before nucleation occurs (i.e., the metastable zone width) and subsequently, to estimate the nucleation rate expressions.

The widths of the metastable zone between temperature range 30-60 °C and various cooling rates range between 0.5-2 °C/min was determined.

Similarly in a same manner, the nucleation in the presence of the crystalline material (i.e., seeds) was determined. The solution was seeded with 0.8 g of crystal (0.275 mm). Afterwards the solution was cooled down to its working saturation temperature.

The degree of supersaturation (i.e., 0.008-kg ammonium perchlorate per kg of water) was justified through the course of the experimental determination of the metastable limits for the seeded solution. This degree of supersaturation was currently matched the increase in solubility of ammonium perchlorate when the temperature of the aqueous solution had increased one degree centigrade.

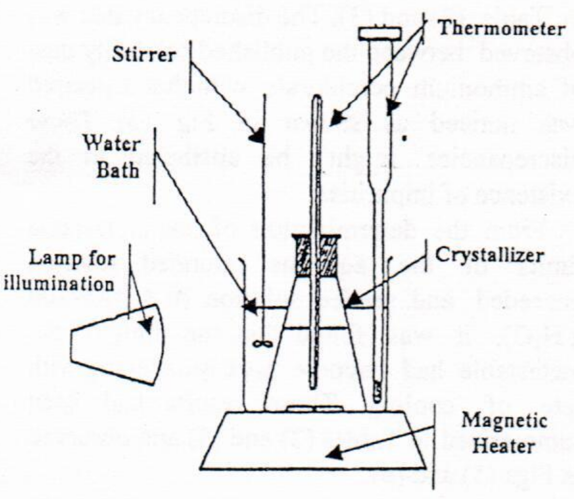
To study the crystal size distribution of ammonium perchlorate, effects of the rate of cooling and isothermal duration time had been investigated. Sieve analysis had been carried out after conducting the crystallization at different rate of cooling using the assembly shown in Fig (3). The size distribution of the produced crystals was determined at specified parameters (i.e., saturation temperature, 50 °C, and agitation speed, 480 rpm that was justified equal to the just suspension velocity). The range of the studied variables are summarized in Table (1) below:

Table (1) Range of rate of cooling and isothermal duration time

Run No.	Rate of Cooling (°C/min)	Isothermal Duration Time (h)
1	0.5	0
2	1.0	0
3	2.0	0
4	1.0	2
5	1.0	4
6	1.0	24

In typical run the saturation was maintained at 15 °C above working temperature. The solution had been cooled to the desired temperature through specified rate of cooling (10 °C below the working saturation temperature). Afterward, the solution had been filtered and the produced crystals had been washed by ether to prevent agglomeration of the crystals. Then the crystals had been placed into an oven. During the first hour of drying the crystals had been shuffled periodically to prevent agglomeration of the crystals. Then crystals were kept over night at 70-80 °C for complete dryness. After that, the dried crystals were subjected to sieve analysis.

To investigate the effect of the isothermal duration time on the median size of the produced crystals, the solution after attaining the desired working temperature 40 °C, was left for different periods under agitation. This period was considered as the isothermal duration time.



Fif. (2) Apparatus for the determination of the metastable zones

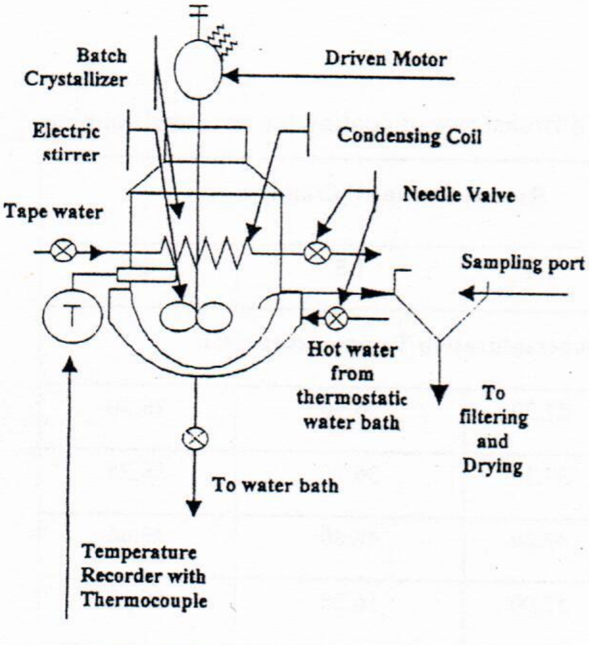


Fig. (3) Layout of the apparatus

Nucleation kinetics determination

It has been frequently suggested by Nyvit (1971) and Mullin (1984) that nucleation rate in bulk system is most conveniently correlated by an expression of the form:

$$R_n = k_n \Delta C^n \qquad (2)$$

Where (k_n) is the mass nucleation rate coefficient and (n) is the order of the process with respect to supersaturation, ΔC.

Measurement of the maximum allowable undercooling for unseeded and seeded solution provide a rapid method for determining primary and secondary nucleation kinetics (Nyvit and Mullin, 1970). Furthermore, the nucleation rate may also be expressed in term of the rate at which supersaturation is created by cooling, viz.

$$R_n = qb \qquad (3)$$

where $b=-dT/dt$, and q is the mass of free solvent present in a dt solution, which is cooled by 1 °C. However, q is a function of concentration and of crystallizing species. Mathematically, this can be expressed in this way:

$$q = \frac{dC^*}{dT} \qquad (4)$$

Where (C) is the solution concentration expressed as mass of anhydrous salt per unit mass of solvent. Meanwhile, maximum allowable supersaturation, ΔC_{max} , may be expressed in term of maximum allowable undercooling, ΔT_{max}:

$$\Delta C_{max} = \left(\frac{dC^*}{dT}\right)\Delta T_{max} \qquad (5)$$

hence eq. (2) can be rewriten to give,

$$\left(\frac{dC^*}{dT}\right)b = k_n\left[\left(\frac{dC^*}{dT}\right)\Delta T_{max}\right]^n \qquad (6)$$

or,

$$\log b = (n-1)\log\left(\frac{dC^*}{dT}\right) + \log k_n + n\log \Delta T_{max} \qquad (7)$$

Which indicate that the dependence of (log b) on (log ΔT_{max}) is linear and the slope of the line gives the order of the nucleation process (n).

The experimental data for the ammonium perchlorate solution over the temperature range between 30 and 60 °C are analyzed with the method of least squares in according to Eq (7).

Accordingly, the nucleation kinetics expression parameters, the nucleation rate constant (k_n) and the order of nucleation (n) could be determined. These parameters are determined at different cooling rate by plotting the maximum allowable under cooling temperature (ΔT_{max}) against rate of cooling.

Eventually, a simple relationship between the concentration and temperature (dC^*/dT) was found equal to 0.008 kg/kg H_2O which represents the slop of the measured solubility curve of ammonium perchlorate. While, the maximum allowable undercooling temperatures (ΔT_{max}) of unseeded and seeded solution are determined from subtracting the measured supersaturation temperature (fogy point of the solution) from saturation temperature.

RESULTS AND DISCUSSION

The solubility curve of our own ammonium perchlorate that was measured in a laboratory assembly was shown in Fig (4) and Tabulated in Table (2) and (3). The discrepancy that was observed between the published solubility data of ammonium perchlorate with that measured was noticed as shown in Fig (5). These discrepancies might be attributed to the existence of impurities.

From the determination of the metastable limits of the aqueous saturated solution unseeded and seeded solution (0.8 gAP/100 g H_2O), it was found that the limit of the metastable had become more broadening with rate of cooling. These results had been summarized in Tables (2) and (3) and observed in Figs (5) and (6).

Table (2) Experimental data for metastable limits at different rate of cooling for unseeded solution

Solubility (g/100 g H_2O)	**Saturation Temperature (°C)**	**Rate of Cooling (°C/min)**			
		0.5	**1.0**	**1.5**	**2.0**
		Supersaturation Temperature (°C)			
26.43	30	28.00	27.30	26.90	26.30
33.33	40	37.80	37.10	36.70	36.25
41.00	50	47.90	47.20	46.80	46.40
49.40	60	57.80	57.00	56.50	56.20

Table (3) Experimental data for metastable limits at different rate of cooling for seeded solution

Solubility (g/100 g H_2O)	**Saturation Temperature (°C)**	**Rate of Cooling (°C/min)**			
		0.5	**1.0**	**1.5**	**2.0**
		Supersaturation Temperature (°C)			
26.43	30	28.80	28.55	28.10	27.45
33.33	40	38.85	38.40	38.00	37.40
41.00	50	48.80	48.40	47.90	47.45
49.40	60	58.75	58.40	57.45	57.35

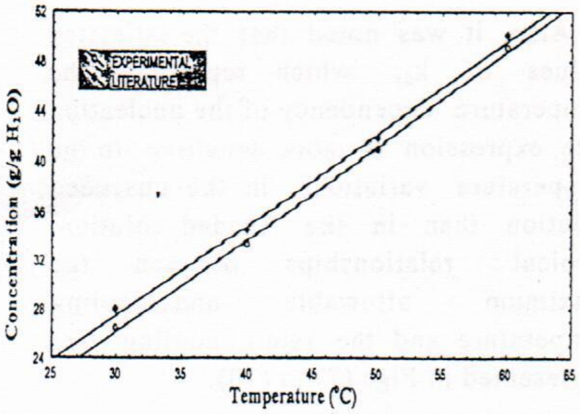


Fig. (4) Measured solubility data of ammonium perchlorate

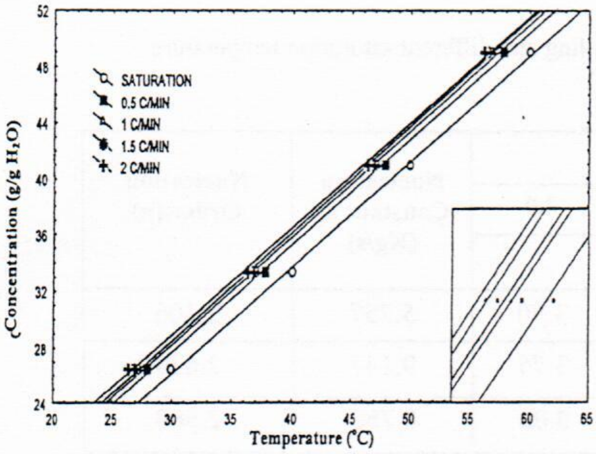


Fig. (5) Metastable limits at different rate of cooling (unseeded solution)

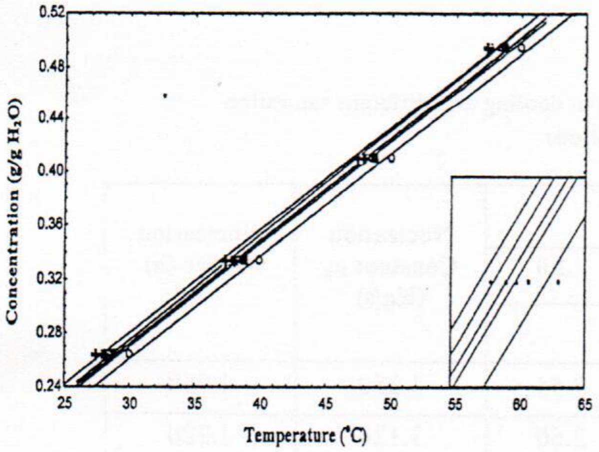


Fig. (6) Metastable limits at different rate of cooling (seeded solution)

Figures (5) and (6) and Tables (2) and (3), shows that the width of the metastable limits become more narrowed for supersaturated solution (seeded) (i.e., 1.20 and 2.65 °C) than the unseeded solution (i.e., 2.00 and 3.80 °C), which was attributed to the existence of the seeds that acts as an initiator (catalyst) for nucleus formation. In other wards, this faster initiating of the seeded solution may also attribute to the attachment of the solution to the seed surface. Mullin (1979) had ascertained this point through his study in the determination of the metastable zones of potassium aluminum sulfate (potash alumina).

The experimental data for the ammonium perchlorate solution over the temperature range 30-60 °C are analyzed with the method of least squares. The parameters of the nucleation expression are determined at different saturation temperature by plotting the maximum allowable under cooling temperature (ΔT_{max}) against rate of cooling. The maximum allowable undercooling temperature and the estimated parameters of the nucleation kinetics expression are summarized in Table (4) and (5).

The results of cooling the seeded and unseeded solutions, Tables (4) and (5), had confirmed that seeds reduces the maximum allowable undercooling temperatures (ΔT_{max}). This observation had coincided with same explanation that was outlined in the determination of the metastable limits for the seeded and unseeded solution. The fact that the order of nucleation order (n) moreover the constants of the nucleation (k_n) for the seeded system, had shown lower values than those for unseeded at a given temperature. This was also come in according to the explanation that contributed to the greater nucleation rate tendency for the unseeded solution in comparison to the seeded solution at a given temperature. The comparison between seeded and unseeded solution and the values of the nucleation parameters had been summarized in Table (6).

The fact that the order of nucleation, n, for the seeded system are lower than those for the unseeded at a given temperature, Table (6), is consistent with the hypothesis submitted by Mullin (1972) that different nucleation mechanisms operate in the two cases. Consequently, faster initiation and lower nucleation would notice in the seeded solution than in the unseeded solution, which might consequently resulted in greater median size crystal in seeded solution process as was noticed later from experimental observation.

Also, it was noted that the estimated values of k_n, which represents the temperature dependency of the nucleation rate expression is more sensitive to the temperature variations in the unseeded solution than in the seeded solution. Typical relationships between the maximum allowable undercooling temperature and the rate of cooling were represented in Figs (7) to (10).

Table (4) Experimental data, (ΔT_{max}) at different rate of cooling and different saturation temperature (unseeded solution)

Saturation Temperature (°C)	**Rate of Cooling (°C/min)**				**Nucleation Constant k_n (Kg/s)**	**Nucleation Order (n)**
	0.5	**1.0**	**1.5**	**2.0**		
	ΔT_{max} (°C)					
30	2.00	2.70	3.10	3.70	5.757	2.306
40	2.20	2.90	3.30	3.75	9,147	2.630
50	2.10	2.80	3.20	3.60	8.786	2.580
60	2.20	3.00	3.50	3.80	7.064	2.500

Table (5) Experimental data, (ΔTmax) at different rate of cooling and different saturation temperature (seeded solution)

Saturation Temperature (°C)	**Rate of Cooling (°C/min)**				**Nucleation Constant k_n (Kg/s)**	**Nucleation Order (n)**
	0.5	**1.0**	**1.5**	**2.0**		
	ΔT_{max} (°C)					
30	1.20	1.45	1.90	2.55	3.350	1.750
40	1.15	1.60	2.00	2.60	3.126	1.720
50	1.20	1.60	2.10	2.55	3.650	1.800
60	1.25	1.60	2.20	2.65	3.270	1.770

Table (6) Values of nucleation parameters for the seeded and unseeded solution

Temperature (°C)	Seeded	k_n	n
30	No	1.088	2.360
40	No	1.540	2.630
50	No	1.517	2.580
60	No	1.192	2.500
30	Yes	0.573	1.750
40	Yes	0.529	1.720
50	Yes	0.632	1.800
60	Yes	0.553	1.770

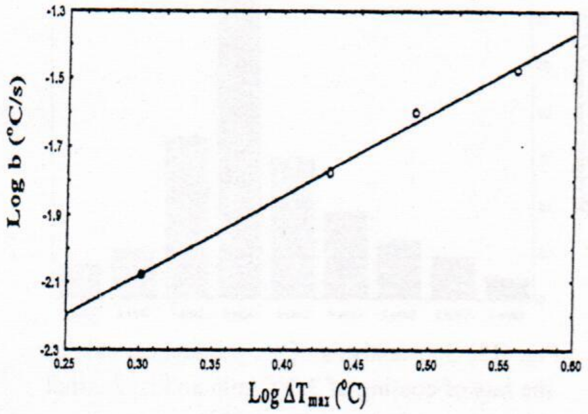


Fig. (7) Effect of cooling rate, b, on the maximum allowable undercooling temperature, ΔT_{max} for unseeded solution (saturation temperature 30°C)

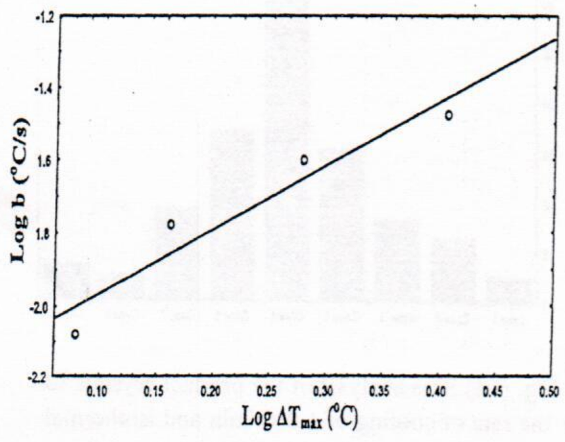


Fig. (8) Effect of cooling rate, b, on the maximum allowable undercooling temperature, ΔT_{max} for unseeded solution (saturation temperature 30°C)

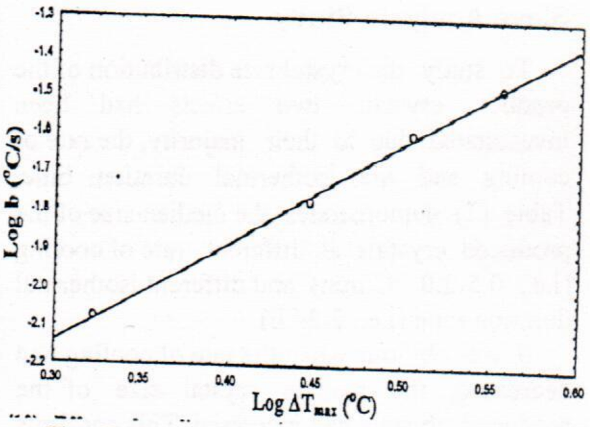


Fig. (9) Effect of cooling rate, b, on the maximum allowable undercooling temperature, ΔT_{max} for unseeded solution (saturation temperature 50°C)

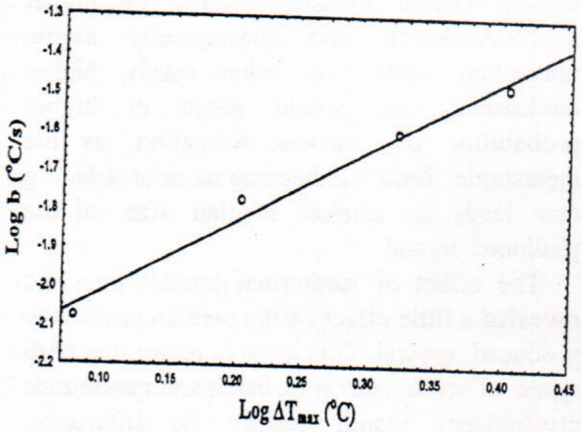


Fig. (10) Effect of cooling rate, b, on the maximum allowable undercooling temperature, ΔT_{max} for unseeded solution (saturation temperature 50°C)

Furthermore, notification was withdrawn from Tables (4) and (5), which stated that at 0.5°C/min cooling rate, minimum value ofAT_{max} for both seeded and unseeded solutions was found for all temperatures. Accordingly, it was concluded that for higher cooling rate, the degree of supersaturation for nucleation was increased which consequently increased the nucleation rate. Eventually, the lesser degree of rate of cooling affected the rate of nucleation in a way that leads to a greater median size of crystals. This was lately ascertained from the observation ensue through studying the effect of the rate of cooling on the crystal size distribution through sieve analysis study.

Sieve Analysis Study

To study the crystal size distribution of the product crystal, two effects had been investigated due to their majority, the rate of cooling and the isothermal duration time. Table (7) demonstrates the median size of the produced crystals at different rate of cooling (i.e., 0.5-2.0 °C/min) and different isothermal duration time (i.e., 2-24 h).

It was obvious when the rate of cooling had decreased, the median crystal size of the produced crystals had increased. This confirms the contributions that submitted through the nucleation kinetics investigation, which was previously stated where higher cooling rate caused broader metastable limits (i.e., higher supersaturation), and consequently higher nucleation rates. In other wards, higher nucleation rate would result in higher probability of nucleus formation, as the metastable limit had become more broadening that leads to smaller median size of the produced crystal.

The effect of isothermal duration time had revealed a little effect on the median size of the produced crystal. This leads in return that both types of crystallizer (i.e., batch and continuous crystallizer) would results no difference. Figure (11) to (16) had shown the sieve analysis of the produced crystals.

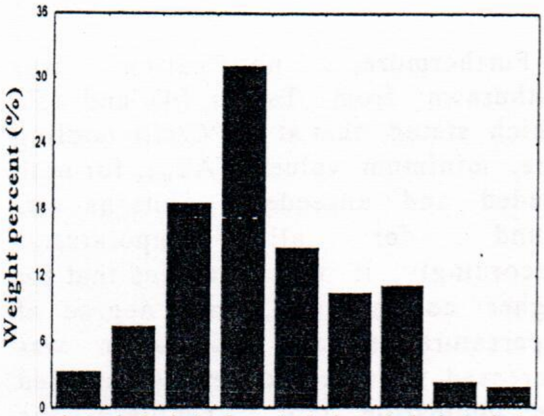


Fig. (11) Size analysis of the product crystals for the rate of cooling of 0.5°C/min and isothermal duration time of 0 hr.

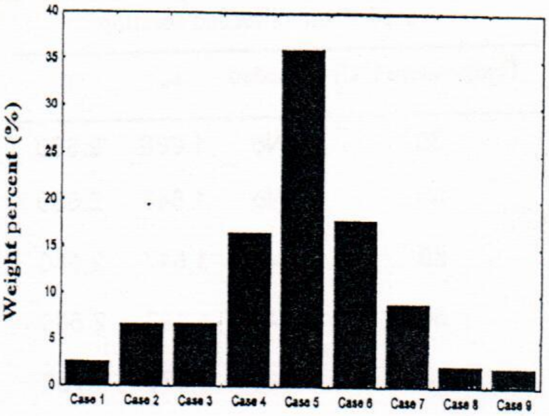


Fig. (12) Size analysis of the product crystals for the rate of cooling of 1.0 °C/min and isothermal duration time of 0 hr.

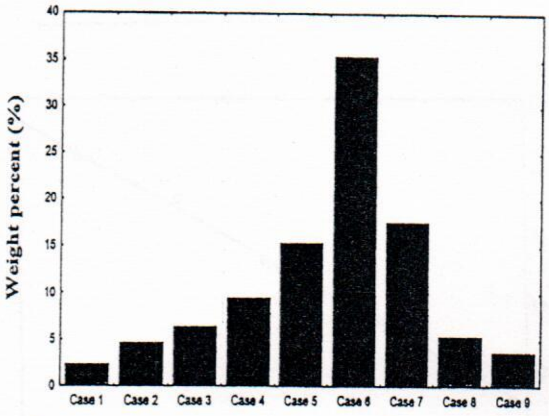


Fig. (13) Size analysis of the product crystals for the rate of cooling of 2.0°C/min and isothermal duration time of 0 hr.

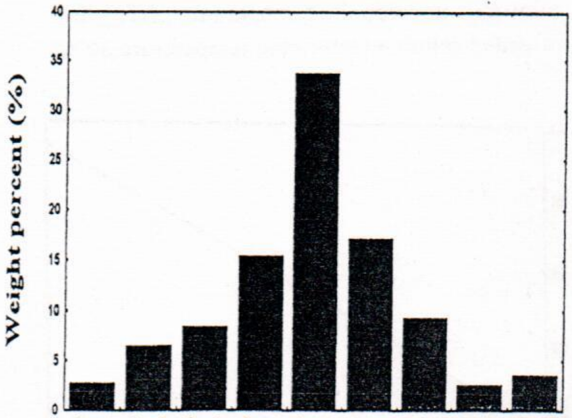


Fig. (14) Size analysis of the product crystals for the rate of cooling of 1.0°C/min and isothermal duration time of 2 hr.

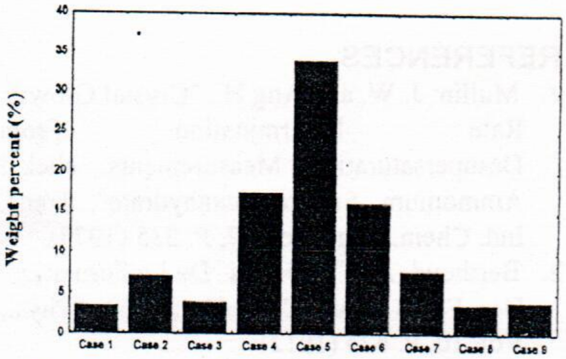


Fig. (15) Size analysis of the product crystals for the rate of cooling of 1.0 °C/min and isothermal duration time of 4 hr.

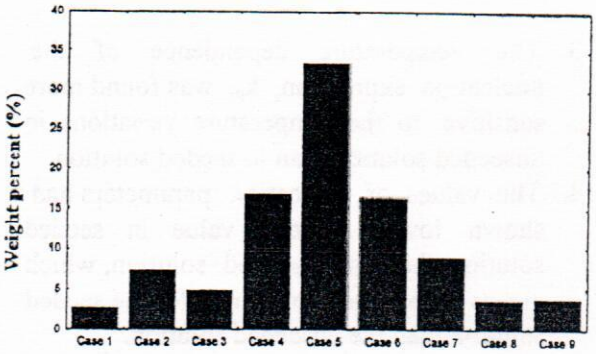


Fig. (16) Size analysis of the product crystals for the rate of cooling of 1.0 °C/min and isothermal duration time of 24 hr.

Table (7) Sieve analysis of produce ammonium perchlorate crystals

Cooling rate °C/min	Isothermal duration Time, h	Crystal size, mm (greater than)									Median size, mm	Total weight, g
		Case 1 1.180	Case 2 0.850	Case 3 0.600	Case 4 0.425	Case 5 0.300	Case 6 0.250	Case 7 0.150	Case 8 0.100	Case 9 0.075		
		Weight percent (%)										
0.5	0	3.20	7.30	18.40	30.90	14.40	10.30	11.00	2.20	1.80	0.430	72.05
1.0	0	2.56	6.55	6.59	16.41	36.05	17.85	8.91	2.26	2.07	0.365	71.95
2.0	0	2.23	4.55	6.32	9.42	15.26	35.26	17.54	5.38	3.58	0.310	72.40
1.0	2	2.70	6.40	8.70	15.26	33.62	16.98	9.20	2.54	3.51	0.360	73.20
1.0	4	3.48	7.10	3.81	17.44	35.93	15.88	7.66	3.60	3.99	0.358	74.15
1.0	24	2.62	7.19	4.74	16.76	33.30	16.30	8.93	3.50	3.70	0.352	75.80

CONCLUSION

The present investigation was mainly concerned with the kinetics of nucleation and crystal growth of ammonium perchlorate from aqueous solution in a laboratory batch cooling crystallizer. Indeed, the parameters of the nucleation kinetics expressions of the seeded and unseeded solutions, isothermal experiments had been evaluated. Their evaluations had been elucidated the most affecting parameters on the crystal growth rates. The studied variables had been manipulated with to examine their effects on the crystal growth rates. These variables had dominated feature for sizing the crystallizer for ammonium perchlorate production and setting up the designation parameters, however, clear distinguishing had been arrived on from the viewpoint of variable dependence on the predominant control model.

Form the experimental work that was conducted in this study, the following conclusions had been attributed:

1. In determining the metastable limits, it was observed that the metastable limits for ammonium perchlorate have relatively narrow limits, e.g. between 2.00 to 3.60 °C for the unseeded solution and between 1.20 to 2.65 °C for the seeded solution.
2. Increasing the rate of cooling, the metastable limits become more broadening for both seeded and unseeded solution. Accordingly, higher rate of cooling gave higher rate of nucleation and consequently smallest median size of the produced crystals.

3. The temperature dependence of the nucleation expression, k_n, was found more sensitive to the temperature variations in unseeded solution than in seeded solution.
4. The values of nucleation parameters had shown lower numeric value in seeded solution than in unseeded solution, which means faster and lower rate for the seeded solution than the unseeded solution.
5. The size distribution study had shown when the rate of cooling had decreased the median crystal size had increased that result in higher probability of nucleus formation, as the metastable limit had become more broadening.
6. The effect of isothermal duration time had revealed a little effect on the median size of the product crystal. Moreover, this leads to; both types of crystallizer (i.e., batch and continuous crystallizer) had shown no difference.

NOMENCLATURE

Symbol	*Definition*	*Units*
b	Rate of cooling	°C
C	Concentration	Kg/;g
C^*	Saturation concentration	Kg/kg
kI	Impurities factor in eq. (2.15)	-
k_n	Rate constant of nucleation	Kg/s
R_G	Overall growth rate	Kg/m^2s
R_n	Overall nucleation rate	Kg/s
T	Temperature	°C
ΔT_{max}	Maximum allowable undercooling temperature	°C

Superscripts	*Definition*	*Units*
b	Mass dependence of nucleation rate	-
C	Size dependence of crystal growth rate	-
E	Solid fraction dependence of the crystal growth rate	-
N	Order of nucleation rate	-

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