CHEMISTRY LETTERS, pp. 489-490, 1994.

A New Type of Kinetic Equation for Crystal Growth Which Can be Applicable to the Second Step of a Two-Step Crystallization of Calcium Hypochlorite Dihydrate

Tsugio MURAKAMI† and Susumu TSUCHIYA
Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube 755

The equation, $dl_a/dt = k\ C_s \exp(-b\ l_a)$, newly proposed can well express the rate of crystal growth in the second step of two-step crystallization of calcium hypochlorite dihydrate.

A new crystallization method to obtain coarse crystals, the shape of which are either double truncated pyramidal, or thick square plate, has recently been proposed.[1] In this method the crystals of calcium hypochlorite dihydrate have been grown by two different steps. In the first step, cylindrical crystals were prepared in a vessel by the addition of a habit modifier, because thin tetragonal plate crystals usually formed without the habit modifier. The cylindrical crystals were then introduced into the other vessel as seeds to be grown. In the second step, double truncated pyramid crystals were grown from the seeds, and the size of crystals obtained was much larger than that formed by old methods, where the thin tetragonal plate crystals grew.

The kinetic analysis of crystals growth is of importance in crystallization to obtain the crystals in a certain size range. Several kinetic equations have been so far proposed,[2] and the kinetic analyses of conventional crystallization methods have been carried out by these equations. These equations, however, could not be applied to the second step of the two-step crystallization. In this paper, we propose a new type of equation, which can be applicable to the crystal growth in the second step, and demonstrate its suitability.

A glass separable flask (500 ml) with an agitator was used for the present experiments. The supersaturated solution in which $Ca(ClO)_2$ (5-6 wt-%) and $CaCl_2$ (30-32 wt-%) were solved was first introduced into the flask. The solution in the flask was kept at 303 K, and under the pH =9.0 ± 0.2. The slurry of cylindrical seed crystals (10.0 - 12.0 wt-%) was then introduced into the solution to start growing the crystals (the concentration of introduced seed crystals of 0.01 - 0.02 wt-%).

The growing processes of the cylindrical seed crystals were followed by an optical-microscope. The photo pictures of the analytical samples obtained during the course of the crystal growth at suitable intervals were taken by the optical-microscope to estimate the average diameter of crystals. Because the observed styles of the cylindrical crystals were either vertical, inclined, or lied, it is therefore reasonable to choose only the lied crystals of them to estimate the average diameter. In the estimation, more than fifty samples of crystals lied were measured. The concentration of supersaturation in the solution was estimated in such a way that the saturation

† Present address : TOSOH Corp., Sinnanyo 746.

amount of calcium hypochlorite was subtracted from that actually solved. The solid-liquid separation of the analytical samples was performed by a high speed centrifugal setting machine.

We propose a model of crystallization on the basis of the following assumptions:

1) A set of Ca^{2+}, $2(ClO)^-$ and $2H_2O$ is considered as a solute molecule, $Ca(ClO)_2{\cdot}2H_2O$. 2) Although there are a certain number of sites on a crystal surface, only one site will be first considered. 3) A solute molecule in a solution approaches the surface of crystal to be adsorbed and deposited on the site, and to immediately become a part of crystal. 4) The new deposited molecule becomes again a site, on which another new molecule can be adsorbed and piled. 5) The adsorption becomes energetically difficult in exponential way with increasing the height of the pile. 6) There are a lot of sites, on which a variety of piles with many kinds of length stand to form a crystal; the crystal is considered as an assembly of piles.

In the present system, the average crystal size can be expressed by l_a and l_c, since $l_a=l_b$, where l_i (i=a, b and c) is the average length of crystals of i-direction. In the two-step crystal growth method, the crystal growth of a-direction was suppressed in the first step. Therefore the crystals markedly grow in a-direction in the second step. Since the ratio of l_a to l_c in the crystal growth without habit modifier is known, the final length of a-direction, l_{af}, could be estimated from the initial length of c-direction, l_c. The length, l_a, would increase with time until l_a eventually become to be l_{af}.

The rate of growth of crystals can be represented by that of increase of l_a, and is reasonably expressed as Eq. (1).

$$dl_a/dt = k\,C_s \exp(-a\,l_a/l_{af}) \qquad (1)$$

where Cs is the concentration of supersaturation in the solution, while k and a are constants. This equation has been derived in a way that is analogous to Zeldovich equation employed for adsorption. Eq. 1 can be varied to be Eq. (2).

$$dl_a/dt = k\,C_s \exp(-b\,l_a) \qquad (2)$$

where $-a/l_{af} = b$.

Figure 1 shows the plot of ln $[(dl_a/dt)/C_s]$ vs. l_a. The experimental results are well expressed by the plot. The value of b and k were calculated to be 0.017 and 130, respectively.

It is accordingly concluded that the Eq. (2) is applicable to express the rate of the crystal growth in the second-step of the two-step crystallization of calcium hypochlorite dihydrate.

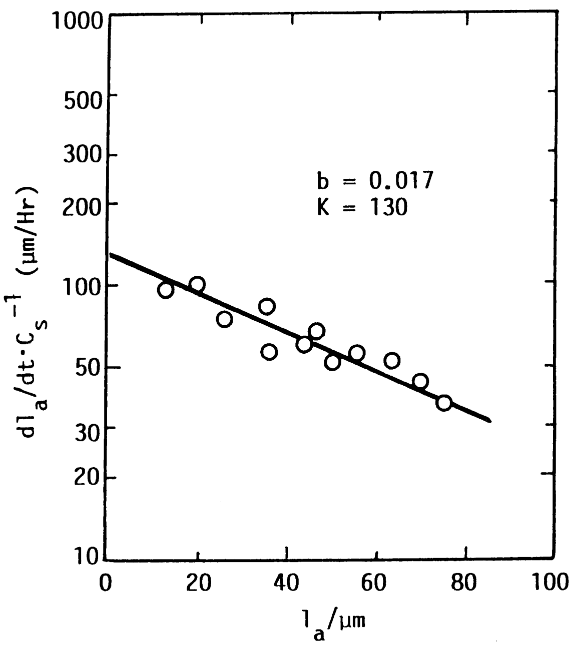

Fig. 1. The plot of ln$[(dl_a/dt)/C_s]$ vs. l_a.

References

1) T. Murakami, M. Kikuchi, K. Igawa, and S. Tsuchiya, 26th Autumn Meeting, Chem. Eng. Soc. Jpn., Kyoto, October 1993, Abstr.II, No. A206.

2) e. g. J. W. Mullin, "Crystallization," 3rd ed , Butterworth-Heinemann, London (1993).

(Received November 26,1993)