

Thermal decomposition kinetics and mechanism of magnesium bicarbonate aqueous solution

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Abstract

Thermal decomposition kinetics and mechanism of magnesium bicarbonate in aqueous solution were investigated. Decomposition rate function, $f(\eta) = 1 - 2/3\eta - (1 - \eta)^{2/3}$, was found to fit well with Ginstling–Brounshtein's diffusion model. The good linearity relationship of rate equation $1 - 2/3\eta - (1 - \eta)^{2/3}$ against time further validated that decomposition process of magnesium bicarbonate was partially controlled by the mode of diffusion. The apparent activation energy was calculated to be 47.05 kJ/mol, indicating that the overall decomposition process was also controlled by chemical reactions. The kinetic model was in good agreement with the experimental results. The effect of stirring speed, system temperature and the concentration of Mg^{2+} in $Mg(HCO_3)_2$ aqueous solution on decomposition ratio was analyzed. The decomposition ratio reached 88% at 50 °C. The formed basic magnesium carbonate was of microsphere structure. The mechanism of thermal decomposition of $Mg(HCO_3)_2$ was proposed in this paper.

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Keywords: Magnesium bicarbonate; Decomposition; Kinetics; Microsphere

1. Introduction

Magnesium oxide (MgO) or magnesia, one of the most important raw materials in the refractory industry, is of high refractoriness (melting point of 2800 °C), corrosion resistance and fire retardant. The presence of this oxide in refractory materials increases the performance of pre-shaped linings for steel production (Amer, 1996). It is also applied widely as a very important chemical raw material. High purity MgO was generally produced from dolomite (Samtani et al., 2002; Caceres and Attiogbe, 1997; Rosa, 1996). Recently, the extensive research has been devoted to the preparation of high purity MgO from magnesite

because of abundant magnesite resources in china (Di, 2001; Zhang and Zhu, 2004). Furthermore, the $MgCO_3$ content in magnesite is over 85%, compared with 30% $MgCO_3$ in dolomite, the cost of MgO production would be greatly reduced. However researchers find that commercial production of MgO from magnesite or dolomite unavoidably involves thermal decomposition and calcination process (Evans and St. Claire, 1949; Smithson and Bakhshi, 1973; Britton et al., 1952a,b; Judd, 1979; Fernández et al., 1999; Morie et al., 1988). Due to the shortage of global energy sources, lowering the energy consumption during any production of magnesium products is the first consideration. By analyzing energy consumption distribution of MgO production process, it is found that about 60% energy consumption is in the thermal decomposition process of $Mg(HCO_3)_2$ aqueous solution as a result of its low Mg^{2+} content at 4.8–7.2 g/L.

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Mass transfer, diffusion and reaction kinetics are important parameters for controlling chemical reaction rate, therefore it is necessary and significant to study decomposition kinetics of $\text{Mg}(\text{HCO}_3)_2$ in aqueous solution for energy saving in commercial production (Fernández et al., 2000; L'vov, 2002; Britton et al., 1952a,b; Powell and Searcy, 1978). In this article, the decomposition mechanism and kinetics are investigated in detail. The decomposition ratio of $\text{Mg}(\text{HCO}_3)_2$ can reach 88% at low temperature of 50 °C, the energy consumption would be greatly reduced compared with conventional thermal decomposition at 100 °C in practical commercial production.

2. Experiment and analysis method

The raw material employed in the experiment was light calcined magnesite, a calcined magnesite residue generated by Shandong Hengxin Magnesite Industry Co. Ltd (Shandong, China) with an average MgO content of 85%, the remainder being CaO , Fe_2O_3 and SiO_2 . The magnesium bicarbonate solution was obtained by carbonization of light calcined magnesite with CO_2 gas at atmospheric pressure. The kinetic decomposition experiments were performed in a 0.5 L 3-neck round bottom flask placed in a thermostat water bath raised to a desired temperature in advance. Magnesium bicarbonate solution was added to the flask. Under continuous stirring of the solution, 3 ml sample was taken from the flask at each predetermined time interval. After immediate filtration, Mg^{2+} concentration in filtrate was determined using EDTA titration method. Following these procedures, the decomposition ratio of magnesium bicarbonate was determined.

The crystal structure of the product was examined using the X-ray powder diffraction (XRD) patterns recorded by a Philips X'Pert diffractometer with Cu-K α radiation. The morphology of MgO microspheres was characterized by Scanning Electron Microscope (SEM, JSM-6301F).

3. Theoretical analysis

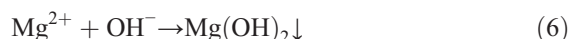
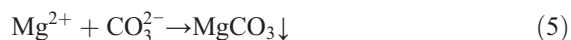
3.1. Chemical reaction

The major chemical reactions involved during the thermal decomposition process of magnesium bicarbonate are as follow,

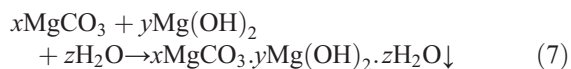
1. Ionization of $\text{Mg}(\text{HCO}_3)_2$



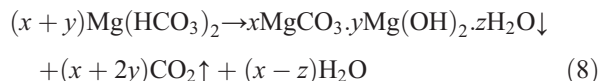
2. Reaction of Mg^{2+} with CO_3^{2-} and OH^-



3. Formation of basic magnesium carbonate



According to above chemical reactions, reactions (2) and (3) can not maintain a steady state. Therefore chemical reaction described in Eqs. (1), (5), (6), and (7) were the rate-determining step. By combination of reaction Eqs. (1)–(7), the overall chemical reaction equation can be written as



The overall chemical reaction rate constant was defined as k' . The escape of CO_2 gas from reaction system would facilitate ionization of $\text{Mg}(\text{HCO}_3)_2$ and formation of basic magnesium carbonate precipitate, which accelerates the thermal decomposition process.

3.2. Kinetic model

The thermal decomposition process of $\text{Mg}(\text{HCO}_3)_2$ includes the formation basic magnesium carbonate precipitates and escape of CO_2 gas from the solution into the air. The decomposition process could be accelerated greatly by constant stirring compared with static decomposition in industrial production. In this study, J is defined as mole quantity of decomposed $\text{Mg}(\text{HCO}_3)_2$ in the solution, S is the total surface area of basic magnesium carbonate particle, C is the concentration of Mg^{2+} in the solution and δ is the diffusion coefficient. We can assume the precipitated particles with the same

size in decomposition process, therefore S is constant. It can be easily shown that (Chen et al., 1998)

$$J = S\delta \frac{dC}{dr} = 4\pi r^2 \delta \frac{dC}{dr} \quad (9)$$

Rearrange of Eq. (9) and integration lead to

$$\frac{J}{4\pi\delta} \int_{r_1}^{r_0} \frac{dr}{r^2} = \int_{C_s}^{C_0} dC \quad (10)$$

For the current chemical reaction system, $C_s \approx C_0$, $C'_s \approx 0$, then mole quantity of decomposed $\text{Mg}(\text{HCO}_3)_2$ in the solution at time t is denoted as follow,

$$J = 4\pi\delta \left(\frac{r_0 r_1}{r_0 - r_1} \right) C_0 \quad (11)$$

At any time t , the mole quantity of precipitated particles (N) can be expressed by

$$N = \frac{4}{3} \pi r_1^3 \frac{\rho}{M} \quad (12)$$

Integration of Eq. (12), then

$$\frac{dN}{dt} = \frac{dN}{dr_1} \frac{dr_1}{dt} = \frac{4\pi\rho r_1^2}{3M} \times \frac{dr_1}{dt} \quad (13)$$

Mole quantity of Mg in the precipitate and in the $\text{Mg}(\text{HCO}_3)_2$ aqueous solution should be equal according to material balance. By analysis of Eq. (8), 1 mol precipitated particles needs to consume $x+y$ mol $\text{Mg}(\text{HCO}_3)_2$, then combining with Eqs.(8), (11), and (12), so

$$J = 4\pi\delta \left(\frac{r_0 r_1}{r_0 - r_1} \right) C_0 = -4\pi(x+y) \frac{\rho}{M} r_1^2 \frac{dr_1}{dt} \quad (14)$$

Rearrange of Eq. (14),

$$-\frac{M\delta C_0}{(x+y)\rho} dt = \frac{r_1(r_0 - r_1)}{r_0} dr_1 = \left(r_1 - \frac{r_1^2}{r_0} \right) dr_1 \quad (15)$$

Integration above Eq. (15), so

$$-\frac{M\delta C_0}{(x+y)\rho} \int_0^t dt = \int_{r_0}^{r_1} \left(r_1 - \frac{r_1^2}{r_0} \right) dr_1 \quad (16)$$

$$-\frac{M\delta C_0}{(x+y)\rho} t = \frac{r_1^2}{2} - \frac{r_0^2}{2} - \frac{r_1^3}{3r_0} + \frac{r_0^3}{3r_0} = \frac{r_1^2}{2} - \frac{r_0^2}{6} - \frac{r_1^3}{3r_0} \quad (17)$$

N_0 is defined as mole quantity of formed basic MgCO_3 particles at time t , while N_I is mole quantity of the initial particles formed at time t_0 . Therefore decomposition ratio (η) can be expressed by mole quantity change of basic magnesium carbonate in the solution, so

$$\eta = \frac{N_0 - N_I}{N_0} \quad (18)$$

Substitute Eq. (12) into Eq. (18), then,

$$\eta = \frac{\frac{4}{3} \times \frac{\pi r_0^3 \rho}{M} - \frac{4}{3} \times \frac{\pi r_1^3 \rho}{M}}{\frac{4}{3} \times \frac{\pi r_0^3 \rho}{M}} = 1 - \frac{r_1^3}{r_0^3} \quad (19)$$

Rearrange Eq. (19) leads to,

$$r_1 = r_0(1 - \eta)^{1/3} \quad (20)$$

Substitute Eq. (20) into Eq. (17), then

$$-\frac{M\delta C_0}{(x+y)\rho} t = \frac{1}{2} r_0^2 (1 - \eta)^{2/3} - \frac{1}{6} r_0^2 - \frac{1}{3} r_0^2 (1 - \eta) \quad (21)$$

By rearranging Eq. (21), so

$$\begin{aligned} \frac{2M\delta C_0}{(x+y)\rho r_0^2} t &= -(1 - \eta)^{2/3} + \frac{1}{3} + \frac{2}{3} (1 - \eta) \\ &= 1 - \frac{2}{3} \eta - (1 - \eta)^{2/3} \end{aligned} \quad (22)$$

Let $k' = \frac{2M\delta C_0}{(x+y)\rho r_0^2}$, then the overall kinetic rate Eq. (23) is obtained, corresponding to Ginstling-Brounshtein's diffusion control model (Li, 2002; Nuñez and Espiell, 1986; Chen et al., 1998).

$$1 - \frac{2}{3} \eta - (1 - \eta)^{2/3} = k' t \quad (23)$$

4. Results and discussion

4.1. Thermal decomposition process

4.1.1. Effect of stirring speed

Due to precipitation of basic magnesium carbonate and formation of CO_2 gas during the decomposition process, the effect of stirring speed on decomposition ratio can not be neglected. Under the experimental conditions of 80 °C and 4.8 g/L Mg^{2+} in solution, the variation of decomposition ratio of $\text{Mg}(\text{HCO}_3)_2$ with stirring speed is shown in Fig. 1. For a reaction time of 50 min and stirring speed over 600 rpm, the increase of decomposition ratio is slow. In contrast, the decomposition ratio increases from 86.0% to 94.2% with the range of stirring speed from 400 to 600 rpm. It appears that the high stirring speed facilitates rapid diffusion of precipitated particles in the solution, makes gas bubbles much smaller and

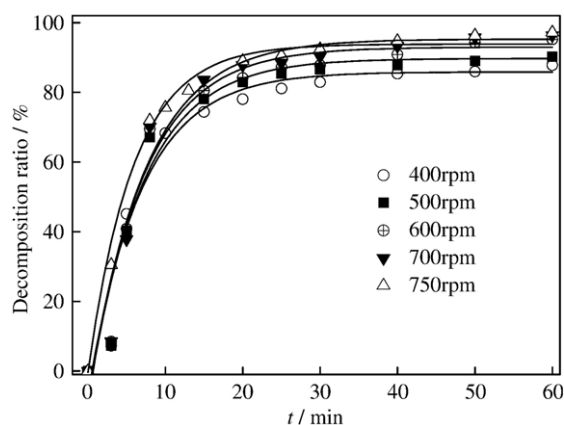


Fig. 1. Effect of stirring speed on the decomposition ratio.

easier to overflow from the solution. As a result, gas–liquid interface and mass transfer are increased greatly, accelerating precipitation reactions. However, when stirring speed is over 700 rpm, its effect on decomposition ratio is marginal. Therefore stirring speed of 600 rpm is chosen for the subsequent kinetics study.

4.1.2. Effect of Mg^{2+} concentration in solution

Maintaining stirring speed at 600 rpm and the system temperature at 80 °C, the effect of Mg^{2+} concentration on decomposition ratio is shown in Fig. 2. When reaction time is over 30 min, maximal decomposition ratios are almost unchanged, indicating that chemical reaction has reached equilibrium within 30 min. With Mg^{2+} concentration of 4.57–5.23 g/L in $Mg(HCO_3)_2$ solution, the curves of decomposition ratio are superposition before 20 min. Then the maximum of decomposition ratio is achieved at 5.23 g/L. However, the maximal ratios are almost the same at Mg^{2+} concentration of 3.00–4.57 g/L, while the decomposition ratio rises rapidly with increasing reactant concentration before 30 min. This can be attributed to rapid precipitation of basic magnesium

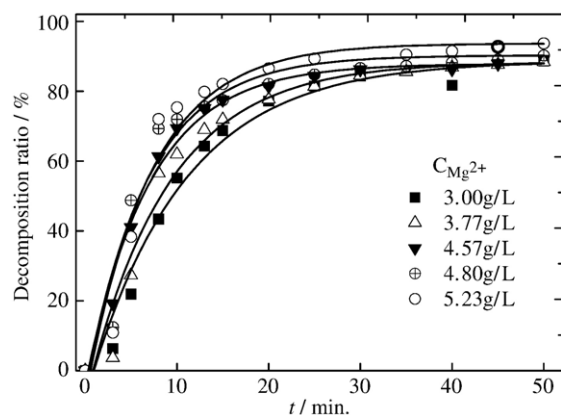


Fig. 2. Effect of Mg^{2+} solution content on the decomposition ratio.

carbonate at the higher reactant concentration. As a result, the increased precipitates in the solution favors reverse reaction. Therefore the optimal concentration of Mg^{2+} in solution is determined at 4.8 g/L.

4.1.3. Effect of reaction temperature

Fixing stirring speed at 600 rpm and Mg^{2+} concentration at 4.8 g/L, the effect of temperature on decomposition ratio is investigated and the results are given in Fig. 3. With increasing system temperature, chemical reaction rate is accelerated and the decomposition ratio is improved greatly, especially in the initial periods of 0–30 min. This finding supports the conclusion that chemical reaction partially controls the decomposition process because raising system temperature results in an increase in chemical reaction rate constant. When system temperature is further increased above 80 °C, the decomposition ratio increases only slightly and the maximum conversion is all above 90%. The variation of decomposition ratio with system temperature is distinct when the system temperature is below 80 °C. In the reaction time of 0–30 min, the decomposition ratios increases quickly with the rise of system temperature from 50 to 80 °C, and then increases slowly to the maximum of 88%–94%. Because the solubility of CO_2 gas would decrease with increasing system temperature, high reaction temperature favors CO_2 gas overflow out of reaction system, which accelerates the chemical reactions. It appears that the diffusion of CO_2 gas in solution controls chemical reaction rate, which consists with the above conclusion of diffusion control. Considering the energy-saving of the thermal decomposition of magnesium bicarbonate, controlling the system temperature at 50 °C is suggested for scale up magnified production.

4.2. Apparent activation energy

Base on above analysis, thermal decomposition kinetics process of magnesium bicarbonate can be verified by the relationship of $f(\eta)$ - t . Furthermore, the relationship between

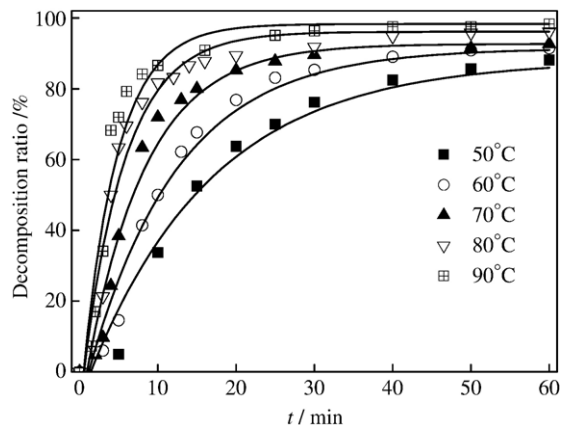


Fig. 3. Effect of system temperature on decomposition ratio.

apparent reaction rate constant k and system temperature T can be expressed in the form of Arrhenius formula

$$k = Z \exp[-E_a/(RT)] \quad (24)$$

Or can be transformed into

$$\ln k = \ln Z - \frac{E_a}{RT} \quad (25)$$

Define $f(\eta)$ as thermal decomposition rate function, according to Eq. (22)

$$f(\eta) = 1 - \frac{2}{3}\eta - (1 - \eta)^{2/3} \quad (26)$$

With Mg^{2+} concentration of 4.8 g/L and stirring speed of 600 rpm, a linear relationship between $f(\eta)$ and t is found with different slope k' , as shown in Fig. 4. The goodness of fit indicates that thermal decomposition process of magnesium bicarbonate is partially controlled by diffusion. From the Arrhenius plot for the reaction rate data k (Fig. 5), calculated from the experiments shown in Fig. 4, the activation energy of 47.05 kJ/mol has been calculated from the slope. Since this value falls above the maximum theoretical value for diffusion control but lower than the usual values for chemical reaction control (Kirk-Othmer, 1995), it could be indicative of chemical-diffusion mixed control for the current systems.

According to chemical reaction Eqs. (1)–(7), the ionization of $\text{Mg}(\text{HCO}_3)_2$ expressed in Eqs. (1)–(4) appears to control chemical reaction rate at the initial stage of thermal decomposition process. As chemical reactions proceed, the interfaces between CO_2 bubbles and the solution are increased due to the increase of CO_2 gas produced. The CO_2 gas is disintegrated into small bubbles which overflow from reaction system because of continuous stirring. The more CO_2 gas escapes from the solution, the faster the thermal decomposition process is, which results in a greater chemical reaction rate. If CO_2 gas can not be diffused in time, reverse reaction will be dominant at the final stage of reactions (3), (5)–(6), which

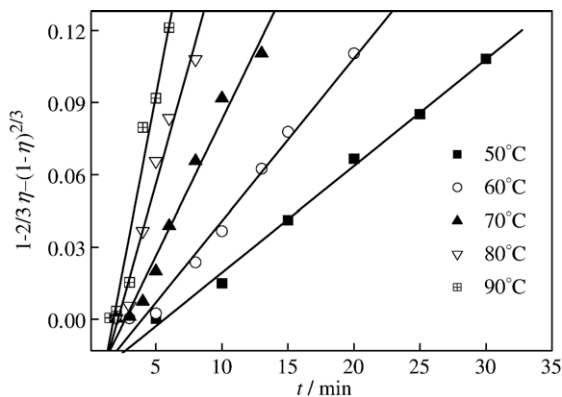


Fig. 4. The plot of $f(\eta)$ against t .

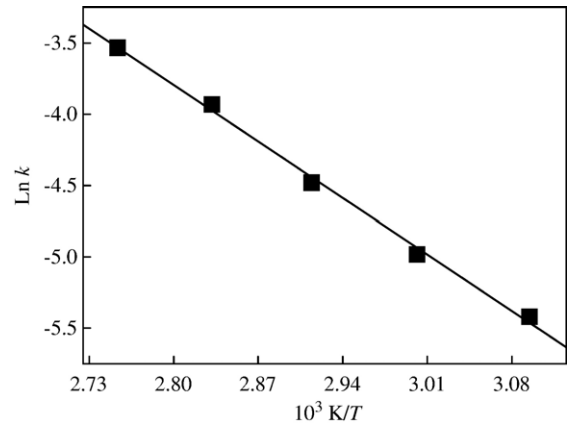


Fig. 5. Arrhenius diagram for determining the activation energy (k data calculated from Fig. 4).

demonstrates that the diffusion rate of CO_2 gas controls partially the decomposition ratio. As a result, the overall thermal decomposition process of $\text{Mg}(\text{HCO}_3)_2$ is controlled by both the diffusion and chemical reaction.

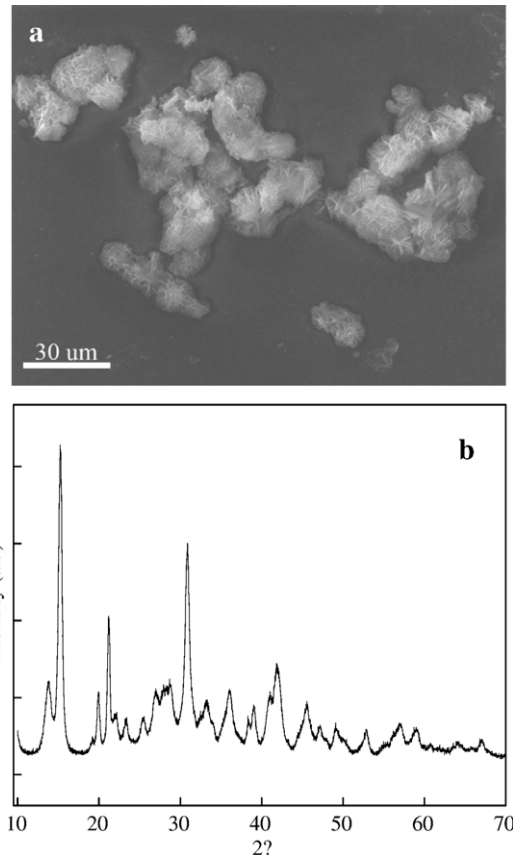


Fig. 6. a is SEM image of the basic magnesium carbonate, and b is its corresponding XRD pattern.

4.3. Characterization of basic magnesium carbonate

Fig. 6a shows SEM image of the basic magnesium carbonate, consisting of microspheres with sheets on the surface. The diameter of the microspheres ranges from 10 μm to 30 μm and the thickness of its sheets is about 30–80 nm. Fig. 6b is the corresponding XRD patterns of basic magnesium carbonate microsphere, showing that all diffraction peaks can be indexed as the monoclinic $4\text{Mg}(\text{CO}_3)\cdot\text{Mg}(\text{OH})_2\cdot 4\text{H}_2\text{O}$. The cell parameters calculated from these diffraction data are $a=10.09$, $b=8.93$, $c=8.35$ Å, and $\beta=113.79^\circ$, which is in good agreement with the reported data (JCPDS file number 25–513). The shape of the peak indicates that the basic magnesium carbonate sample is well crystallized.

5. Conclusions

- 1). The decomposition rate function $f(\eta)$ is determined, $f(\eta)=1-2/3\eta-(1-\eta)^{2/3}$. Thermal decomposition process of magnesium bicarbonate is co-controlled by diffusion and chemical reaction. The apparent activation energy is calculated to be 47.05 kJ mol^{-1} .
- 2). The decomposition mechanism is that the ionization of $\text{Mg}(\text{HCO}_3)_2$ is dominant at the initial reaction period, and then the diffusion rate of CO_2 gas determines chemical reaction rate.
- 3). The optimal thermal decomposition conditions of $\text{Mg}(\text{HCO}_3)_2$ are that the stirring rotation speed is 600 rpm, the concentration of Mg^{2+} in $\text{Mg}(\text{HCO}_3)_2$ solution is 4.8 g/L and system temperature is 50°C .
- 4). Decomposition ratio of $\text{Mg}(\text{HCO}_3)_2$ can reach 88% at 50°C . The formed basic magnesium carbonate consists of many microspheres with sheets on the surface.

Nomenclature

J	Molar quantity of reacted $\text{Mg}(\text{HCO}_3)_2$ in the solution, mol
S	The surface of $(\text{MgCO}_3)_x(\text{Mg}(\text{OH})_2)_y$ particles, m^2
δ	The diffuse coefficient, $\text{m}^2\text{ s}^{-1}$
C	Concentration of Mg^{2+} in the solution at time t , mol L^{-1}
C_S	Original concentration of Mg^{2+} in the solution, mol L^{-1}
C'_S	Final concentration of Mg^{2+} in the solution, mol L^{-1}
r	Precipitation nucleus radius, m
r_0	Precipitation particle radius, m
N	Molar quantity of the precipitated particles, mol
ρ	Density of the precipitated particles, kg m^{-3}

M	Molar weight of the precipitated particles, kg mol^{-1}
η	Decomposition ratio
E_a	Apparent activation energy, kJ mol^{-1}
k'	Overall reaction rate constant, $\text{m}^3\text{ s}^{-1}\text{ L}^{-1}$
k	Slope of $f(\eta)-t$ curve, s^{-1}
R	Universal gas constant, $\text{J mol}^{-1}\text{ K}^{-1}$
t	Time, min
Z	Pre-exponential factor
T	System temperature, K

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