Zhang, Jianxin; Louhi-Kultanen, Marjatta

Determination of nucleation kinetics of cobalt sulfate by measuring metastable zone width and induction time in pure and sulfuric acid solution

Published in:
Powder Technology

DOI:
10.1016/j.powtec.2023.118463

Published: 15/05/2023

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Determination of nucleation kinetics of cobalt sulfate by measuring metastable zone width and induction time in pure and sulfuric acid solution

Jianxin Zhang, Marjatta Louhi-Kultanen*

Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, 02150 Espoo, Finland

HIGHLIGHTS

- Nucleation rate of cobalt sulfate by metastability and induction time studies.
- Sulfuric acid promotes nucleation of cobalt sulfate.
- Sulfuric acid decreases particle size and changes crystal shape.
- Raman and UV–visible spectroscopy successfully applied for solubility measurements.

GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
Cobalt sulfate
Sulfuric acid
Nucleation kinetics
Metastable zone width
Induction time
Solubility

ABSTRACT

The metastable zone width (MSZW) and induction time of CoSO₄ in the presence of H₂SO₄ were measured at various operating conditions by polythermal and isothermal methods, respectively. Raman spectroscopy and UV–Vis have been successfully adopted for measuring the solubility of CoSO₄. The nucleation parameters were estimated with a self-consistent Nývlt-like approach and classical 3D theory approach. The results show a decrease in the solubility of CoSO₄ with an increase in the concentration of H₂SO₄. MSZW decreased when raising the saturation temperature, mixing speed, and H₂SO₄ concentration, and decreasing the cooling rate. The induction time measurement indicated that the system showed homogeneous nucleation at high supersaturation (>1.15) and heterogeneous nucleation at low supersaturation (<1.15). The crystallized product was CoSO₄·7H₂O which has an octahedron shape and cubic shape with and without H₂SO₄, respectively. Moreover, the particle sizes are smaller with increased H₂SO₄ concentration and cooling rate.

* Corresponding author.
E-mail address: marjatta.louhi-kultanen@aalto.fi (M. Louhi-Kultanen).

https://doi.org/10.1016/j.powtec.2023.118463
Received 26 January 2023; Received in revised form 16 March 2023; Accepted 17 March 2023
Available online 20 March 2023
0032-5910/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
1. Introduction

Cobalt (Co) has been recognized as one of the critical raw materials because of the continuously increased demand and the uncertainty surrounding the supply of primary cobalt [1–5]. To ease the additional pressures on the supply chain of Co and achieve a more circular economy, cobalt recovery from secondary resources is a timely crucial topic. The hydrometallurgical process is predominant in cobalt recovery due to its high selectivity, high metal extraction, and low-energy consumption [6,7]. In the hydrometallurgical processes, cobalt is recovered from the cobalt-containing solutions obtained after leaching and purification [8–10]. Typically, cobalt could be recovered as cobalt metal by electro-winning, as cobalt salts (CoSO₄, Co(OH)₂, and CoCO₃) by precipitation or crystallization, and as metal powder by H₂ reduction.

CoSO₄ is one of the most common products in cobalt manufacture. In the cobalt production process, cobalt frequently exists as cobalt sulfate in solution, since sulfuric acid is widely utilized as a leaching or strip agent [11–14]. Moreover, cobalt sulfate is an important raw material in the production of NCM (Ni-Co-Mn) or NCA (Ni-Co-Al) lithium-ion batteries and other cobalt salts [15–17]. Evaporative crystallization is conventionally employed for the production of cobalt sulfate. The biggest disadvantage of evaporative crystallization is the massive energy consumption due to the large latent heat of water evaporation, although improvements now exist for minimizing the energy demand, including multi-effect evaporation and mechanical vapor recompression crystallization [18,19]. Furthermore, the acidic streams generated in evaporative crystallization can cause equipment corrosion. Therefore, an alternative process for CoSO₄ manufacture could be cooling crystallization due to the temperature sensitivity of cobalt sulfate solubility.

During the crystallization process, nucleation kinetics play a vital role in producing the CoSO₄ crystal with sufficient quality, target PSD, and purity at minimum cost. It is necessary to design and optimize the cooling crystallization following the kinetic parameters, which can be studied by measuring the metastable zone width (MSZW) and induction time [20–22]. Moreover, operation is normally considered to be optimal when cooling crystallization is carried out within the metastable zone. MSZW is affected by many parameters, such as saturation temperature, mixing speed, the cooling program, and impurities [23–26]. For CoSO₄, however, no previous studies have reported the kinetics of CoSO₄ cooling crystallization, even though cooling crystallization has been applied in the industrial field.

Therefore, the aim of the present work was to crystallize CoSO₄ on laboratory scale and estimate the kinetic parameters by using different theoretical approaches based on the measured MSZW and induction time with unseeded batch cooling crystallization. In addition, the influence of the temperature range, cooling rate, mixing speed, and the sulfuric acid concentration on the MSZW and induction time were investigated.

2. Materials and methods

2.1. Materials and apparatus

The chemicals used were of analytical purity grade, CoSO₄·7H₂O (>99 wt%, Sigma-Aldrich Inc.) and H₂SO₄ (98 wt%, Sigma-Aldrich Inc.). All chemicals were used without further purification and all solutions were prepared using deionized water.

An EasyMax 402 stirred tank system (Mettler Toledo) with a 100 mL glass reactor was used for batch cooling crystallization. The solution in the reactor was mixed using a pitched-blade turbine with four blades (Φ = 38 mm). The temperature was adjusted and monitored using iControl software with a temperature measurement accuracy of ±0.01 K. In addition, focused beam reflectance measurement (FBRM, Particle Track G400) was employed to detect nucleation by monitoring the crystal number with the following instrument operating parameters: scanning speed of 2 m/s, and data recording every 10 s. The crystallizer is shown in Fig. 1.

2.2. Measurements of solubility

The solid-liquid equilibrium values of the CoSO₄·H₂SO₄·H₂O system were determined by the isothermal method in the temperature range of 278.15 to 313.15 K and H₂SO₄ concentration range of 0 to 0.6 molality. First, saturated solutions were prepared by adding an excess of solid CoSO₄·7H₂O and dissolving the major part in the H₂SO₄ solution with a specific concentration. The suspensions were then kept at the target temperature and stirred for a sufficient time (48 h) to reach equilibrium. Finally, the solution samples were collected by filtration for measuring the cobalt and sulfate concentrations. Three parallel experiments for each condition were carried out.

2.2.1. UV–Vis measurement

The cobalt concentration was measured with a UV–Vis spectrophotometer (HACH, DR 6000). For a UV–visible spectrophotometer, the light absorbance (Abs) is directly proportional to the molecular concentration, molar absorptivity, and path length of the light through the sample [27,28]. Malik et al. [29] reported that the peak at 512 nm could be assigned to cobalt. In this study, the absorbance at 512 nm was used for cobalt concentration analysis. Prior to the cobalt concentration measurement, a calibration model for the relationship between absorbance and cobalt concentration was built by measuring the absorbance of the cobalt standard solutions at concentration range of 0.01 to 0.5 mol/L. The measurements were carried out with a 10 mm path length quartz cuvette. The scan range was set in between 200 and 900 nm with

Fig. 1. Schematic diagram of the experimental setup.
a scan speed of 240 nm/min. Each sample was measured three times to
determine the average value. The UV–Vis spectra of cobalt calibration
solutions are shown in Fig. 2 (a), and the calibration curve and model are
shown in Fig. 2 (b). It can be seen from the high values of the correlation
coefficient $R^2$ that the calibration model is reasonably accurate. Pre-
dictions of cobalt concentration were always done with the calibration
model that had the same measurement conditions. The Co concentration
could be calculated with following Eqs. (1) and (2).

$$C_{Co} \left( \frac{\text{mol}}{L} \right) = \left[ \frac{(Abs - 0.0227)}{4.898} \right] \times D$$  \hspace{1cm} (1)

where, Abs is the UV–Vis absorbance peak at 512 nm for Co; $D$ is the
dilution factor; $\rho$ is the density of solutions without dilution measured by
density meter (DMA 5000 M, Anton Paar), g/cm$^3$; $M_{CoSO_4}$ is the molar
mass of cobalt sulfate (155 g/mol); $M_{H_2SO_4}$ is the molar mass of sulfuric
acid (98 g/mol).

2.2.2. Raman measurement

For sulfate concentration analysis, a Raman spectrometer (Renishaw
inVia™) was utilized. The quantity of $SO_4^{2-}$ was determined with a
calibration model based on the ratio of the peak area at 980 cm$^{-1}$ and
the internal standard of the peak area of the water bond (1643 cm$^{-1}$)
[30,31]. In the present study, a calibration was built using cobalt sulfate
standard solutions in concentration range between 0.065 and 0.830
mol/L. The Raman spectra of standard solutions and the calibration
model are shown in Fig. 2 (c) and (d), respectively. In the Raman
measurements, a green laser with the wavelength of 532 nm was used.
The laser beam was positioned using a Leica imaging microscope with an
x63 immersion objective lens. The spectra were recorded in the range of
300 to 2000 cm$^{-1}$ with an exposure time of 10 s, 25 mW laser power,
and accumulation of five times. Each measurement was repeated three
times. The measurement conditions for samples and calibration solu-
tions were the same. The measured total concentration of sulfate solute

$$C_{Co} (\text{mole fraction}) = \frac{C_{Co} \left( \frac{\text{mol}}{L} \right)}{C_{Co} \left( \frac{\text{mol}}{L} \right) + \left[ \frac{1000\rho - C_{Co} \left( \frac{\text{mol}}{L} \right) \times M_{CoSO_4} - C_{H_2SO_4} \left( \frac{\text{mol}}{L} \right) \times M_{H_2SO_4}}{18 + C_{H_2SO_4} \left( \frac{\text{mol}}{L} \right)} \right]}$$  \hspace{1cm} (2)
covers sulfate ions of cobalt sulfate and sulfuric acid in the mother liquor. The sulfuric acid concentration was calculated based on Eqs. (3)–(5).

\[ C_{SO_4}^− \left( \frac{mol}{L} \right) = \left[ \frac{(PAR - 0.0376)}{2.762} \right] \times D \]  
\[ C_{H_2SO_4} \left( \frac{mol}{L} \right) = C_{SO_4}^− \left( \frac{mol}{L} \right) - C_{Co^2+} \left( \frac{mol}{L} \right) \]  
\[ C_{H_2SO_4} \left( \frac{mol}{kg \text{ water}} \right) = \frac{1000ρ - C_{Co^2+} \left( \frac{mol}{L} \right) \times M_{CoSO_4} - C_{H_2SO_4} \left( \frac{mol}{L} \right) \times M_{H_2SO_4}}{2} \]  

where, PAR is the peak area ratio measured from Raman spectrometer.

### 2.3. Determination of MSZW and induction time

The MSZW of cobalt sulfate in the solution containing water and sulfuric acid was measured with the conventional polythermal technique (Mullin, 2001). The experimental process is as follows: (1) An amount of CoSO₄·H₂SO₄·H₂O suspension was prepared. The suspension was then heated to saturation temperature and kept mixed for 60 min to approach equilibrium, and the undissolved crystals were separated by vacuum filtration. The filtrate (100 g) was placed into the cooling crystallizer; (2) The solution was first heated to 5 K above the saturation temperature for 30 min to ensure that no particles were in the solution, and then cooled at different cooling rates (3, 6, 9, 12, 15 K h⁻¹). As shown in Fig. 3 (a), the nucleation was detected by FBRM based on the increase in count rate. Moreover, the change in solution temperature was also applied for identifying nucleation since the nucleation of cobalt sulfate releases heat and raises the solution temperature. The temperature reaction was recorded as the induction time \( t_{ind} \).

\[ \Delta T_{max} = T_{sat} - T_{nucleation} \]  

For induction time measurements, the isothermal measurement method was applied as shown in Fig. 3(b) [32]. First, the saturated solution of cobalt sulfate with a certain amount of sulfuric acid was prepared at saturation temperature. The solution was heated to a temperature 5 K higher than the saturated temperature and then held there for 30 min. Then, the solution was cooled to the target nucleation temperature \( T_{nucleation} \) as fast as possible and held constant at \( T_{nucleation} \) until nucleation occurred. The corresponding time from the point at which the \( T_{nucleation} \) was reached to the nucleation observed by FBRM and temperature reaction was recorded as the induction time \( t_{ind} \).

### 2.4. Characterization of solid product

To understand the effects of the cooling rate and sulfuric acid concentration on the final product, the characterization of products generated from cooling solutions (303.15 K to 283.15 K) with different cooling rates (3, 6, and 12 K/h) and sulfuric acid concentrations (0, 0.2, 0.4, and 0.6 M) was carried out. The solid products were collected by vacuum filtration after washing twice the filter cake with a saturated ethanol solution. The crystals phases were characterized using a Panalytical X’Pert Pro diffractometer with Cu Kα1 radiation (λ = 1.5406 Å) operated at 40 kV. The morphology of the products was examined using an Olympus BX53M optical microscope. The particle size distribution (PSD) was analyzed with a Malvern Master Sizer 2000 laser diffraction particle size analyzer. In addition, a TGA (thermal gravimetric analysis, Q 500, TA instruments) was applied for thermal properties analysis. The TGA analysis, approximately 10 mg of the sample was loaded into a platinum pan and heated to 500 °C at a rate of 10 °C/min. Analysis was conducted under a nitrogen purge with a 60 mL/min flow.

### 3. Theoretical approaches for nucleation kinetics estimation

#### 3.1. Theoretical approaches based on MSZW

To explain the relationships between MSZW and various factors such as temperature, cooling rate, and mixing speed, both the self-consistent Nývlt-like approach and classical 3D nucleation approach are frequently adopted.

#### 3.1.1. Self-consistent Nývlt-like approach

Nývlt’s eq. [33] has been widely used to estimate nucleation kinetics because of its simplicity. However, the units of obtained apparent nucleation order and constant are so complicated that their physical meaning still remains obscure. In order to address this situation, Sangwal et al. [34–36] proposed the self-consistent Nývlt-like approach. In this approach, the nucleation rate \( J \) was redefined as the following power-law equation:

\[ J = K(\ln S)^m \]  

where \( K \) is the new nucleation constant (#/(m³·s)), \( m \) is the apparent order of nucleation, and \( S \) is the relative supersaturation.

Using the regular solution theory, the ln S could be expressed by the maximum temperature difference as Eq. (8):
\[
\ln S = \ln \left( \frac{C_{\text{sat}}}{C_{\text{mol}}} \right) = \left( \frac{\Delta H_d}{RgT_{\text{nucl}}} \right) \frac{\Delta T_{\text{sat}}}{T_{\text{sat}}} \tag{8}
\]

where \(C_{\text{sat}}\) is the solubility at saturation temperature \(T_{\text{sat}}\), \(C_{\text{mol}}\) is the solubility at nucleation temperature \(T_{\text{nucl}}\), \(\Delta H_d\) and \(Rg\) denote the dissolution enthalpy and the universal gas constant, 8.314 J K\(^{-1}\) mol\(^{-1}\).

Sangwal proposed the following linear relationship between the cooling rate \(R\) and maximum supercooling ratio \(\Delta T_{\text{max}}/T_{\text{sat}}\):

\[
\ln \left( \frac{\Delta T_{\text{max}}}{T_{\text{sat}}} \right) = \varphi + \beta \ln R \tag{9}
\]

where

\[
\beta = 1/m
\]

\[
\varphi = \frac{1 - m}{m} \ln \left( \frac{\Delta H_d}{RgT_{\text{nucl}}} \right) + \frac{1}{m} \ln \left( \frac{f}{K} \right) + \frac{1}{m} \ln (T_{\text{sat}})
\]

\[
(10)
\]

Therefore, Eq. (9) predicts the linear dependence of \(\ln (\Delta T_{\text{max}}/T_{\text{sat}})\) on \(\ln R\). The term \(\Delta H_d/RgT_{\text{nucl}}\) can be calculated from the solubility data; the values of nucleation order \(m\) and the term \(f/K\) can be calculated from the slope \(\beta\) and the intercept \(\varphi\), respectively. Constant \(f\) representing the number of particles per volume (\#/m\(^3\)) was calculated by substituting solubility at a certain temperature in Eq. (12).

\[
f = C_{\text{coba}} \left( \frac{\text{mol}}{L} \right) \times 1000 \times N_A \tag{12}
\]

where \(N_A\) is the Avogadro number, 6.02 \times 10\(^{23}\) mol\(^{-1}\).

Moreover, Sangwal [36] proposed that the value of \(\varphi\) is associated with the saturation temperature \(T_{\text{sat}}\). The relationship between \(\varphi\) and \(T_{\text{sat}}\) can be expressed by Eq. (13):

\[
-\varphi = -\varphi_0 - \frac{E_{\text{sat}}}{RgT_{\text{sat}}} \tag{13}
\]

where the pre-exponential factor \(-\varphi_0\) is the extrapolated value of \(-\varphi\) corresponding to \(T_{\text{sat}} = \infty\), and \(E_{\text{sat}}\) is the activation energy for the formation of crystallites in the solution.

### 3.1.2. Classical 3D nucleation approach

Based on the classical theory of 3D nucleation [37], Sangwal [38] proposed an approach for estimating the nucleation kinetics by using MSZW data. Unlike Eq. (7), a different relationship between nucleation rate \(J\) and supersaturation is adopted in this approach, as Eq. (14):

\[
J = A \exp \left[ -\frac{B}{(\ln S)^2} \right] \tag{14}
\]

Here, \(A\) is a pre-exponential factor (\#/m\(^3\) s) and \(B\) is a thermodynamic parameter related to the nuclei formation, which could be given by Eq. (15):

\[
B = \frac{16\gamma^3}{3} \left( \frac{\Omega^2}{k_BT_{\text{sat}}} \right)^3 \tag{15}
\]

where \(\gamma\) is the solid-liquid interfacial energy, \(k_B\) is the Boltzmann constant (1.380649 \times 10\(^{-23}\) J K\(^{-1}\)), \(\Omega\) represents the molecular volume of the solute: 2.396 \times 10\(^{-28}\) (m\(^3\)/mol) for CoSO\(_4\)-7H\(_2\)O which calculated by Eq. (16).

\[
\Omega = \left( \frac{M_{\text{CoSO}_4-7\text{H}_2\text{O}}}{\rho_{\text{CoSO}_4-7\text{H}_2\text{O}}} \times 10^{-6} \right) \times N_A \tag{16}
\]

where \(M_{\text{CoSO}_4-7\text{H}_2\text{O}}\) is the molar mass of CoSO\(_4\)-7H\(_2\)O, 281.1 g/mol; \(\rho_{\text{CoSO}_4-7\text{H}_2\text{O}}\) is the density of solid CoSO\(_4\)-7H\(_2\)O, 1.948 g/cm\(^3\).

Combining the above equation set, Sangwal [45] suggests a new linear relationship between the \((T_{\text{sat}}/\Delta T_{\text{max}})^2\) and \(\ln R\), written as Eq. (17):

\[
\left( \frac{T_{\text{sat}}}{\Delta T_{\text{max}}} \right)^2 = F - F_1 \ln R \tag{17}
\]

where

\[
F_1 = \frac{1}{B} \left( \frac{\Delta H_d}{RgT_{\text{sat}}} \right) = \frac{3}{16\pi} \left( \frac{k_BT_{\text{sat}}}{\Omega^2} \right)^3 \left( \frac{\Delta H_d}{RgT_{\text{sat}}} \right)^2 \tag{18}
\]

\[
F = F_1 \ln \left( \frac{A}{f \cdot \Delta H_d/RgT_{\text{sat}}} \right) \tag{19}
\]

With Eq. (18), the values of interfacial energy \(\gamma\) and \(A/f\) can be estimated from the slope \(F_1\) and the intercept \(F\), respectively. Like the self-consistent Nyvlt-like approach, the intercept \(F\) is also dependent on the saturation temperature \(T_{\text{sat}}\), and Sangwal [36] suggested an Arrhenius-type equation to describe the relationship between the \(\ln (F^2/5)\) and \(T_{\text{sat}}\), as Eq. (20). The activation energy for the formation of crystals in solution could be estimated by using Eq. (20).

\[
\ln (F^2) = \left[ \ln (F) \right]^2 + \frac{E_{\text{sat}}}{RgT_{\text{sat}}} \tag{20}
\]

#### 3.2. Theoretical approach based on induction time

It is usually assumed that the induction time \((t_{\text{ind}})\) is inversely proportional to the nucleation rate \((J)\) [39], which could be given as

\[
t_{\text{ind}} = k/J \tag{21}
\]

Combining Eqs. (14), (15), and (21), the relationship between the induction time and supersaturation could be expressed as Eq. (22):

\[
\ln(t_{\text{ind}}) = K + \frac{16\gamma^3}{3k_BT} \left( \ln S \right)^2 \tag{22}
\]

here, there is a linear relationship for plotting \(\ln(t_{\text{ind}})\) against \(1/(\ln S)^2\) at a constant temperature. The slope \(b\) of the straight line is

\[
b = \frac{16\gamma^3k_T^2}{3k_BT} \tag{23}
\]

Therefore, the interfacial energy \(\gamma\) could be obtained by the slope \(b\) as Eq. (24):

\[
\gamma = \left( \frac{3b}{16\pi} \right)^{1/3} \tag{24}
\]
Powder Technology 422 (2023) 118463

Δenthalpy for cobalt sulfate in solutions with different sulfuric acid concentrations increased within the range of 0 to 0.6 M, the solubility continuously decreased. That may be because of the common ion effect of SO₄²⁻ which dissociated from the sulfuric acid and cobalt sulfate. Based on the temperature dependence of solubility in Fig. 4, an Arrhenius-type plot of ln C against 1/T was built for solubility prediction and dissolution enthalpy calculation, as shown in Eq. (25):
\[
\ln C = \ln(A_1) - \frac{\Delta H_d}{R} \left(\frac{1}{T}\right)
\]

where C is the cobalt sulfate solubility (molar fraction), T is the solution temperature (K), and ln (A₁) is an empirical constant. The dissolution enthalpy for cobalt sulfate in solutions with different sulfuric acid concentrations are calculated and listed in Table 1. Table 1 shows, that the dissolution enthalpy for cobalt sulfate solutions increases with the sulfuric acid concentration increase. With the equation and parameter values shown in Table 1, the CoSO₄ solubility in sulfuric acid solution in the temperature range of 273.15 K to 313.15 K could be estimated. The obtained correlation coefficient values show that the models have very good accuracy for solubility prediction.

4. Results and discussion

4.1. Solubility of CoSO₄₆ in sulfuric acid solutions

Although the solubility of cobalt sulfate in pure water has already been reported in the literature, there are few solubility data regarding CoSO₄ related to sulfuric acid solutions. Here, cobalt sulfate solubilities in sulfuric acid solutions were investigated with sulfuric acid concentration in the range of 0 to 0.6 molality and at a temperature from 273.15 to 313.15 K. The measured solubility data and data from the literature are shown in Fig. 4. It can be seen that the measured solubility in pure water agrees well with the literature data [39–41], which proves the accuracy of the applied research methodology. The solubility increased with a temperature increase. By contrast, with the sulfuric acid concentration increasing within the range of 0 to 0.6 M, the solubility continuously decreased. That may be because of the common ion effect of SO₄²⁻ which dissociated from the sulfuric acid and cobalt sulfate. Based on the temperature dependence of solubility in Fig. 4, an Arrhenius-type plot of ln C against 1/T was built for solubility prediction and dissolution enthalpy calculation, as shown in Eq. (25):
\[
\ln C = \ln(A_1) - \frac{\Delta H_d}{R} \left(\frac{1}{T}\right)
\]

where C is the cobalt sulfate solubility (molar fraction), T is the solution temperature (K), and ln (A₁) is an empirical constant. The dissolution enthalpy for cobalt sulfate in solutions with different sulfuric acid concentrations are calculated and listed in Table 1. Table 1 shows, that the dissolution enthalpy for cobalt sulfate solutions increases with the sulfuric acid concentration increase. With the equation and parameter values shown in Table 1, the CoSO₄ solubility in sulfuric acid solution in the temperature range of 273.15 K to 313.15 K could be estimated. The obtained correlation coefficient values show that the models have very good accuracy for solubility prediction.

4.2. MSZW measurements

4.2.1. Effects of cooling rate and saturation temperature on the MSZW

As shown in Fig. 5, the MSZW of a CoSO₄ aqueous solution was detected by the temperature increase and FBRM. It shows that the MSZW widens with an increase in the cooling rate from 3 K/h to 15 K/h, thus enhancing the nucleation and narrowing the MSZW.

4.2.2. Effect of mixing speed on MSZW

The effect of the mixing speed on the nucleation temperature and MSZW were studied by varying the mixing speed from 300 rpm to 500 rpm. The solution was cooled down from the saturated temperature of 298.15 K at a constant cooling rate of 12 K/h until nucleation occurred and was detected by the temperature increase and FBRM. The results are shown in Table 2. The MSZW of the CoSO₄ aqueous solution apparently decreases with the increase in stirring rate from 300 rpm to 500 rpm. Since the agitation has a synergistic effect by increasing the heat and mass transportation and the collisions in the solution, the greater mixing speed seems to enhance the nucleation and decrease the MSZW.

4.2.3. Effect of sulfuric acid concentration on MSZW

The initial saturated solution was prepared at a temperature of 303.15 K, based on the measured solubility data shown in Fig. 4. The concentrations of sulfuric acid used varied between 0 and 0.6 molality. The effect of the sulfuric acid concentration on the MSZW was studied at a constant cooling rate of 12 K/h and mixing speed of 300 rpm, and the results are shown in Table 3. The MSZW of cobalt sulfate solution becomes slightly narrower with the increase in sulfuric acid concentration. The effects of the sulfuric acid concentration on the MSZW could be explained by two possible reasons. One is that the addition of sulfuric acid changes the solubility of cobalt sulfate, as shown in Fig. 4. Based on the solubility prediction model illustrated in Section 3.1 and Eq. (8), it is

---

**Table 1**

<table>
<thead>
<tr>
<th>Sulfuric acid concentration (M)</th>
<th>ln A₁</th>
<th>ΔH_d (J/mol)</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.276</td>
<td>10,981.96</td>
<td>0.998</td>
</tr>
<tr>
<td>0.1</td>
<td>1.209</td>
<td>10,873.05</td>
<td>0.997</td>
</tr>
<tr>
<td>0.2</td>
<td>1.164</td>
<td>12,832.66</td>
<td>0.995</td>
</tr>
<tr>
<td>0.4</td>
<td>1.889</td>
<td>12,712.11</td>
<td>0.996</td>
</tr>
<tr>
<td>0.6</td>
<td>2.281</td>
<td>13,781.96</td>
<td>0.995</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Mixing speed Rpm (Tip speed, m/s)</th>
<th>T_nuc (K)</th>
<th>ΔT_max (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 (0.60)</td>
<td>281.07 ± 0.38</td>
<td>17.08 ± 0.38</td>
</tr>
<tr>
<td>400 (0.80)</td>
<td>281.99 ± 0.43</td>
<td>16.16 ± 0.43</td>
</tr>
<tr>
<td>500 (1.00)</td>
<td>282.71 ± 0.51</td>
<td>15.44 ± 0.51</td>
</tr>
</tbody>
</table>

Note: Data expressed as mean ± SD (n = 3).

**Table 3**

<table>
<thead>
<tr>
<th>Sulfuric acid concentration mol/kg water</th>
<th>T_nuc (K)</th>
<th>ΔT_max (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>287.95 ± 0.59</td>
<td>15.20 ± 0.59</td>
</tr>
<tr>
<td>0.1</td>
<td>288.09 ± 0.73</td>
<td>15.06 ± 0.73</td>
</tr>
<tr>
<td>0.2</td>
<td>288.56 ± 0.51</td>
<td>14.59 ± 0.51</td>
</tr>
<tr>
<td>0.4</td>
<td>288.93 ± 0.43</td>
<td>14.22 ± 0.43</td>
</tr>
<tr>
<td>0.6</td>
<td>289.22 ± 0.48</td>
<td>13.93 ± 0.48</td>
</tr>
</tbody>
</table>

Note: Data expressed as mean ± SD (n = 3).
7

Table 4
Induction of cobalt sulfate with different sulfuric acid concentrations under same undercooling (ΔT = Tsat − Tnucl = 303.15−293.15 = 10 K).

<table>
<thead>
<tr>
<th>Sulfuric acid concentration mol/kg water</th>
<th>tind (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>153</td>
</tr>
<tr>
<td>0.1</td>
<td>127</td>
</tr>
<tr>
<td>0.2</td>
<td>68</td>
</tr>
<tr>
<td>0.4</td>
<td>64</td>
</tr>
<tr>
<td>0.6</td>
<td>46</td>
</tr>
</tbody>
</table>

Fig. 6. Induction time of cobalt sulfate under different supersaturation levels and nucleation temperature at 293.15 K to 303.15 K with aqueous CoSO₄ solutions (mixing speed is 300 rpm).

measure the induction time as a function of supersaturation. Three different nucleation temperatures (293.15, 298.15, and 303.15 K) were selected and different supersaturation levels were obtained by varying the undercooling degree. The results are presented in Fig. 6. As expected, the induction time decreases considerably with increasing supersaturation. In addition, with the rising nucleation temperature, the induction time shows a significant decrease. The effects of sulfuric acid concentration on the induction time were also studied by cooling the solution from the saturation temperature of 303.15 K to the nucleation temperature of 293.15 K, which is an undercooling of 10 K. The results are shown in Table 4. The induction time decreases continuously with the increase in sulfuric acid concentration. The results agree with the MSZW measurement given in Section 4.2.3. The induction time decrease is caused by the increase in supersaturation levels and possibly by the solution structure change due to the addition of sulfuric acid.

4.4. Nucleation kinetics of cobalt sulfate in pure solution by analyzing MSZW

According to the experimental MSZW results shown above in Fig. 5, the parameters of nucleation kinetics could be estimated by using the two theoretical approaches described in Section 3.1. Since the nucleation rate (J), pre-exponential factor (A), and nucleation constant (K) are represented with unit of #/m² s, the unit of K/s was used for cooling rate R in the calculations.

4.4.1. Self-consistent Nývlt-like approach to estimate the nucleation kinetics

According to the self-consistent Nývlt equation (Eqs. (7)–(11)), ln (ΔTmax/Tsat) is plotted against ln R from the data in Fig. 5 to calculate the nucleation parameters at different saturation temperatures and a constant mixing speed of 300 rpm, as shown in Fig. 7(a). The linear relationship between ln (ΔTmax/Tsat) and ln R could be established by using the self-consistent Nývlt-like approach. Further, it gives a good fit of the experimental data for five different temperatures, with a correlation coefficient of 0.937, 0.940, 0.976, 0.993, and 0.973 for 293.15 K, 298.15 K, 303.15 K, 308.15 K, and 313.15 K, respectively. The kinetic parameters determined by the self-consistent Nývlt-like approach are listed in Table 5. The apparent nucleation order m shows a decrease from 2.266 to 1.249 with the increased saturation temperature. The results satisfy the rules published by Nývlt et al. [43] that the apparent nucleation order for inorganic compounds lies between 0.98 and 8.3. Furthermore, the results show that the values of nucleation constant K at different saturation temperatures are about the same and independent of the saturation temperature. Based on the parameters listed in Table 5, the nucleation rate J with different saturation temperatures and supersaturations could be calculated based on Eq. (7), and the results are

![Fig. 7. Plots of ln(ΔTmax/Tsat) versus ln R (a, left) and (Tsat/ΔTmax)² versus ln R (b, right) at different saturation temperatures with the same mixing speed of 300 rpm (tip) with pure CoSO₄ solutions.](image-url)
plotted in Fig. S1. The figure shows that the nucleation rate increases with an increase in the saturation temperature at the same supersaturation level. The relationship between parameter \( \varphi \) and \( T_{\text{sat}} \) could be applied for activation energy estimation as expressed by Eq. (13). The plot of \( -\varphi \) against \( 1/T_{\text{sat}} \) is shown in Fig. 8. The linear relationship is established with a correlation coefficient value of 0.904. The activation energy \( E_{\text{sat}} \) is 41.14 kJ/mol, calculated based on Eq. (13).

4.4.2. Classical 3D nucleation approach to estimate the nucleation kinetics

According to the classical 3D nucleation approach (Eqs. (14)–(19)), \((\Delta T_{\text{max}}/T_{\text{sat}})^2\) is plotted against \( \ln R \) and a linear relationship is established from the data in Fig. 5, as shown in Fig. 7(b). This approach also provides a good fit with the experimental data on the cobalt sulfate for different saturation temperatures, with a correlation coefficient value of 0.985, 0.979, 0.907, 0.912, and 0.964 for 293.15 K, 298.15 K, 303.15 K, 308.15 K, and 313.15 K, respectively. The nucleation kinetic parameters, such as \( F, F_1, A, B, \) and \( \gamma \), are estimated from the experimental data and the values are listed in Table 6. The parameters \( F_1 \) and \( F \) are both sensitive to the saturation temperature, increasing with the rising saturation temperature. This result suggests that the kinetic parameter \( A \) increases with an increase in the saturation temperature. Therefore, a higher saturation temperature could accelerate the nucleation rate due to the high generation of supersaturation and faster mass and energy transformation. This explains why the MSZW narrows with an increase in saturation temperature. Furthermore, the interfacial energy \( \gamma \) shows a decrease with a rise in saturation temperature. This result demonstrates that a higher saturation temperature might make the nucleation process occur more easily. Based on the results shown in Table 6, the nucleation rates were calculated with Eq. (14), as shown in Fig. S1(b). From Fig. S1(b), the nucleation rate is increased with rising the saturation temperature at the same supersaturation. Moreover, it was clearly found that nucleation needs a higher supersaturation for lower saturation temperature. As Sangwal et al. proposed, the plot of \( \ln (F_1/2) \) as a function of \( 1/(\ln S)^2 \) was performed for each nucleation temperature, as shown in Fig. 9. The interfacial energy for different nucleation temperatures under homogeneous nucleation are listed in Table 7.

![Fig. 8. Plot of \( -\varphi \) versus \( 1/T_{\text{sat}} \) for self-consistent N\"yvt-like approach aqueous CoSO\(_4\) solutions.](image)

Table 5

<table>
<thead>
<tr>
<th>( T_{\text{sat}} ) (K)</th>
<th>( m - 1/\beta )</th>
<th>( \varphi )</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>2.028</td>
<td>-0.070</td>
<td>0.937</td>
</tr>
<tr>
<td>298.15</td>
<td>1.946</td>
<td>-0.024</td>
<td>0.972</td>
</tr>
<tr>
<td>303.15</td>
<td>1.667</td>
<td>0.418</td>
<td>0.976</td>
</tr>
<tr>
<td>308.15</td>
<td>1.548</td>
<td>0.523</td>
<td>0.993</td>
</tr>
<tr>
<td>313.15</td>
<td>1.249</td>
<td>1.009</td>
<td>0.973</td>
</tr>
</tbody>
</table>

\[ E_{\text{sat}} = 41.14 \text{ kJ/mol} \]

<table>
<thead>
<tr>
<th>( T_{\text{sat}} ) (K)</th>
<th>( m - 1/\beta )</th>
<th>( \varphi )</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>2.028</td>
<td>-0.070</td>
<td>0.937</td>
</tr>
<tr>
<td>298.15</td>
<td>1.946</td>
<td>-0.024</td>
<td>0.972</td>
</tr>
<tr>
<td>303.15</td>
<td>1.667</td>
<td>0.418</td>
<td>0.976</td>
</tr>
<tr>
<td>308.15</td>
<td>1.548</td>
<td>0.523</td>
<td>0.993</td>
</tr>
<tr>
<td>313.15</td>
<td>1.249</td>
<td>1.009</td>
<td>0.973</td>
</tr>
</tbody>
</table>

\[ E_{\text{sat}} = 41.14 \text{ kJ/mol} \]

Table 6

<table>
<thead>
<tr>
<th>( T_{\text{sat}} ) (K)</th>
<th>( F )</th>
<th>( F_1 )</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>-2813.10</td>
<td>552.17</td>
<td>0.985</td>
</tr>
<tr>
<td>298.15</td>
<td>-3832.00</td>
<td>737.17</td>
<td>0.979</td>
</tr>
<tr>
<td>303.15</td>
<td>-6505.70</td>
<td>1205.80</td>
<td>0.907</td>
</tr>
<tr>
<td>308.15</td>
<td>-10,221.00</td>
<td>1880.60</td>
<td>0.912</td>
</tr>
<tr>
<td>313.15</td>
<td>-31,164.00</td>
<td>5681.30</td>
<td>0.964</td>
</tr>
</tbody>
</table>

\[ B = 4.506, \quad \Delta H_d/(R T_{\text{sat}}) = 3.974, \quad A = 10^{26}, \quad \gamma = 1.363 \]

Table 7

<table>
<thead>
<tr>
<th>( T_{\text{nuclt}} ) (K)</th>
<th>( b )</th>
<th>( \gamma ) (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.187</td>
<td>2.345</td>
</tr>
<tr>
<td>298.15</td>
<td>0.159</td>
<td>2.303</td>
</tr>
<tr>
<td>303.15</td>
<td>0.148</td>
<td>2.240</td>
</tr>
</tbody>
</table>
T_{\text{sat}} could be used to determine the activation energy according to Eq. (20). However, the calculated values of parameters of \( F \) in the present study are all negative which cannot be applied in Eq. (20) for activation energy.

4.5. Nucleation kinetics of cobalt sulfate by analyzing induction time

The relationships between the induction time \( t_{\text{ind}} \) and supersaturation \( S \) at three different nucleation temperatures are shown in Fig. 9. Based on the results obtained, two nucleation mechanism regions can be identified based on the supersaturation level [44]. The heterogeneous primary nucleation could be the dominating mechanism at lower supersaturation (\( S < 1.15; (ln S)^{-2} > 51 \)), whereas the homogeneous primary nucleation is the most important phenomenon in unseeded batch crystallization at supersaturation >1.15. Based on the homogeneous nucleation mechanism, the value of the interfacial energy was determined based on the slope \( b \) of the straight lines, and the results are listed in Table 7. The \( \gamma \) shows a slight decrease with an increase in nucleation temperature, indicating that nucleation occurs more readily at higher temperatures, i.e., an increase in the nucleation temperature favors the formation of the crystal nucleus.

4.6. Crystal characterization

The products obtained by cooling from 303.15 K to 283.15 K with different cooling rates (3, 6, and 12 K/h) and sulfuric acid concentrations (0, 0.2, 0.4, and 0.6 M) were characterized by XRD, optical microscopy, and Malvern laser diffraction analysis. The XRD results in Fig. 10 show that the crystallized products are cobalt sulfate heptahydrate in both pure cobalt sulfate solution and in the solution with sulfuric acid addition. Although some peaks at 2\( \theta \) of 15\( ^{\circ} \), 26\( ^{\circ} \), and 37\( ^{\circ} \) referring to the planes of (200), (4 0 0), and (−3 1 4) respectively disappeared, the addition of sulfuric acid did not change the hydrate forms.

Fig. 10. XRD pattern of products crystallized from solutions of different sulfuric acid concentrations.

Fig. 11. Optical microscopy image of products crystallized a) from aqueous solution and b) from 0.2 mol/dm\(^3\) sulfuric acid concentration.

Fig. 12. PSD of products crystallized with different: (a) cooling rates; (b) sulfuric acid concentrations.
of the crystals. The TG-DTG analyses for samples obtained from pure cobalt sulfate solution and solution with 0.2 M sulfuric acid were carried out and the results are shown in Fig. 13. The total weight losses during the heating process for both samples were about 44% which is close to the theoretical weight losses for the dehydration of CoSO₄·7H₂O. The TG-DTG results also showed that the dehydration of CoSO₄·7H₂O has several stages with the temperature increase and dehydration to hexahydrate occurs at a relative low temperature about 40 °C. The crystal images are shown in Fig. 11. The particles obtained from the pure cobalt sulfate solution are mostly octahedron in shape, whereas the particles obtained from the solution with 0.2 M sulfuric acid are close to cubic in shape and their aggregation tendency can be seen more clearly. Fig. 12 illustrates the PSD for different cooling rates and sulfuric acid concentrations. It is clear that the PSD becomes smaller, from an average size of 498 μm to 296 μm, when the sulfuric acid concentration increased from 0 to 0.6 molality. Moreover, the PSD decreased with an increased cooling rate because of the increasing supersaturation levels at the nucleation temperature. When the cooling rate increased, the MSZW become wider that the nucleation occurs at a lower nucleation temperature and the supersaturation of nucleation increased.

5. Conclusions

The nucleation kinetics of cobalt sulfate was investigated by measuring the solubility, MSZW, and induction time in aqueous solutions and in sulfuric acid solutions with concentrations of 0 to 0.6 molality during unseeded batch cooling crystallization. In the solubility measurements, Raman spectroscopy and UV–Vis spectrophotometry were applied for the analysis of sulfate ion and cobalt ion, respectively. The FBRM and temperature increase were both adopted for detecting the occurrence of nucleation.

The solubility of cobalt sulfate shows an increase with temperature, whereas it decreases with a rise in sulfuric acid concentration. The MSZW narrows with an increase in saturation temperature and mixing speed. Sulfuric acid shows the promotion of CoSO₄ nucleation in such a manner that increasing the sulfuric acid concentration decreases the MSZW slightly. Based on the self-consistent Nyvlt-like approach, the parameter μ decreases with an increase in the saturation temperature, while the nucleation order gradually decreases with an increase in the saturation temperature from 2.266 to 1.249. Based on the classical 3D nucleation approach, both parameters F and FI show increases with the rise in saturation temperature. When the saturation temperature increased, the interfacial energy showed a decrease, meaning that it is easier to nucleate at higher temperatures, which is consistent with the narrowing of the MSZW as the saturation temperature rises. Besides, the activation energy 𝑊𝑡ind of the cobalt sulfate nucleation process obtained from the self-consistent Nyvlt-like approach is 41.14 kJ/mol, whereas the parameters F calculated from classical 3D nucleation approach are negative that cannot be applied for the activation energy calculation. These results give a suggestion that the unit for cooling rate has a significant influence on the calculation of kinetic parameters.

The induction time was measured for different supersaturation levels, nucleation temperatures, and sulfuric acid concentrations. The induction time decreased with increasing supersaturation, temperature, and sulfuric acid concentration. For the pure cobalt sulfate solution, the homogeneous primary nucleation dominated at high primary supersaturation (S > 1.15), and heterogeneous primary nucleation dominated at low supersaturation (S < 1.15). In addition, the interfacial energy of cobalt sulfate decreased slightly with an increase in the nucleation temperature. Above all, the estimated nucleation kinetic parameters are extremely valuable in the design and development of a crystallization process.

Symbol list

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-exponential factor (#/m³·s)</td>
</tr>
<tr>
<td>A₁</td>
<td>Empirical constant for solubility estimation</td>
</tr>
<tr>
<td>B</td>
<td>Thermodynamic parameter</td>
</tr>
<tr>
<td>b</td>
<td>Slope for interfacial energy calculation based on induction time</td>
</tr>
<tr>
<td>C</td>
<td>Cobalt sulfate solubility (mol fraction)</td>
</tr>
<tr>
<td>Csat</td>
<td>Cobalt sulfate solubility at saturation temperature (mol fraction)</td>
</tr>
<tr>
<td>Cnuc</td>
<td>Cobalt sulfate solubility at nucleation temperature (mol fraction)</td>
</tr>
<tr>
<td>Eₙuc</td>
<td>Activation energy for the nucleation (J/mol)</td>
</tr>
<tr>
<td>F</td>
<td>Intercept in Classical 3D nucleation approach</td>
</tr>
<tr>
<td>FI</td>
<td>Slope in Classical 3D nucleation approach</td>
</tr>
<tr>
<td>f</td>
<td>Proportionality constant (#/m³)</td>
</tr>
<tr>
<td>ΔH_d</td>
<td>Dissolution enthalpy (J/mol)</td>
</tr>
<tr>
<td>J</td>
<td>Nucleation rate (#/m³·s)</td>
</tr>
<tr>
<td>K</td>
<td>Nucleation constant (#/m³·s)</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzmann constant (1.380649 × 10⁻²³ J·K⁻¹)</td>
</tr>
<tr>
<td>M</td>
<td>Molality (mol solute/kg water)</td>
</tr>
<tr>
<td>MCoSO₄·7H₂O</td>
<td>Molar mass of cobalt sulfate heptahydrate (281.1 g/mol)</td>
</tr>
<tr>
<td>m</td>
<td>Apparent nucleation order</td>
</tr>
<tr>
<td>R</td>
<td>Cooling rate (K/s)</td>
</tr>
<tr>
<td>Rg</td>
<td>Gas constant (8.314 J·K⁻¹·mol⁻¹)</td>
</tr>
<tr>
<td>S</td>
<td>Relative supersaturation (−)</td>
</tr>
<tr>
<td>T</td>
<td>Solution temperature (K)</td>
</tr>
<tr>
<td>Tₙuc</td>
<td>Temperature of saturation solution (K)</td>
</tr>
<tr>
<td>Tmax</td>
<td>Nucleation temperature of solution (K)</td>
</tr>
<tr>
<td>ΔT_max</td>
<td>Metastable zone width (K)</td>
</tr>
<tr>
<td>tₙuc</td>
<td>Induction time (min)</td>
</tr>
<tr>
<td>μ</td>
<td>Slope in self-consistent Nyvlt-like approach</td>
</tr>
<tr>
<td>r</td>
<td>Solid-liquid interfacial energy (J/m²)</td>
</tr>
</tbody>
</table>
References


Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.powtec.2023.118463.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Zhang Jianxin wishes to acknowledge the funding from CSC, China (China Scholarship Council, No. 201806370220). The authors would also like to thank Chemobrionics COST Action CA17120, Belgium. This work made use of Aalto University Bioeconomy and RawMatters Facilities.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.powtec.2023.118463.

J. Zhang and M. Louhi-Kultanen


