Recovering Cobalt from Aqueous Solutions by Evaporative, Reactive, and Cooling Crystallization

Jianxin Zhang
Recovering Cobalt from Aqueous Solutions by Evaporative, Reactive, and Cooling Crystallization

Jianxin Zhang

A doctoral thesis completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Engineering, at a public examination held at the lecture hall Ke2 of the school on 22nd of March 2024 at 10 o'clock.

Aalto University
School of Chemical Engineering
Department of Chemical and Metallurgical Engineering
Chemical Engineering in Aqueous System
Supervising professor
Professor Marjatta Louhi-Kultanen, Aalto University, Finland

Thesis advisors
Professor Marjatta Louhi-Kultanen, Aalto University, Finland
Professor Daniel Lindberg, Aalto University, Finland

Preliminary examiners
Docent Mikael Svärd, KTH Royal Institute of Technology, Sweden
Professor Hongxun Hao, Tianjin University, China

Opponent
Professor Zoltan Nagy, Purdue University USA/Loughborough University UK

Aalto University publication series
DOCTORAL THESES 58/2024

© 2024 Jianxin Zhang

ISBN 978-952-64-1724-0 (printed)
ISBN 978-952-64-1725-7 (pdf)
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

Unigrafia Oy
Helsinki 2024

Finland
Abstract

With the challenge of climate change, the restructuring of transportation and power sectors is crucial for achieving greenhouse gas neutrality. Cobalt, which plays a key role in the energy transition, has been recognized as one of the critical materials globally. The hydrometallurgical process has shown great potential in extracting cobalt from both primary and secondary resources during cobalt manufacture. Recovering cobalt from aqueous solutions is an essential step in the hydrometallurgy process of cobalt extraction.

Crystallization is a separation and purification technology by forming solids from solutions. In this study, the recovery of cobalt salts from aqueous cobalt sulfate solution using vacuum evaporative crystallization, cooling crystallization, and carbonate precipitation was investigated. The thermodynamic data includes the saturation vapor pressure for cobalt sulfate solution and the cobalt sulfate solubility in aqueous solutions was determined. The effects of operational conditions on crystallization and final products were indicated by recovering cobalt sulfate through vacuum evaporative crystallization, batch, and continuous cooling crystallization. At temperatures below 40 °C, cobalt sulfate primarily crystallizes in the heptahydrate form, while at temperatures of 60 and 80 °C, it crystallizes in the hexahydrate form. The CoSO₄·7H₂O is prone to dehydration during the drying process. Additionally, the primary nucleation kinetics of CoSO₄ were determined by measuring the solubility, metastable zone width (MSZW), and induction time in batch cooling crystallization. The secondary nucleation dominated crystalline cobalt sulfate in a continuous cooling crystallization were also investigated based on the Mixed-Suspension, Mixed-Product-Removal (MSMPR) theory, and Population balance equations (PBEs). In addition, operation conditions like temperature, mixing speed, and impurities significantly affect the crystal size and crystallization kinetics.

In the cobalt carbonate precipitation, the precipitation mechanism was successfully investigated using inline Focused Beam Reflectance Measurement (FBRM) and pH monitoring and offline measurement (Scanning electron microscope, X-ray powder diffraction, Raman spectroscopy). With the pH decreasing, the cobalt initially precipitated as Co₃CO₃(OH)₉ and continuously transferred to CoCO₃. Raman spectrometry has been found to a great potential in studying the crystallization of metal salts for both solid phase identification and ionic concentration quantification. Moreover, UV-Vis spectrophotometry is efficient for the quantitative analysis of cobalt and nickel concentrations in solutions.
Acknowledgements

The research presented in this thesis was carried out during the years 2019-2023 in the research group of Chemical Engineering in Aqueous Systems at Aalto University (School of Chemical Engineering). This work has been supported by the China Scholarship Council (CSC, No. 201806370220), and by Chemobrionics COST Action CA17120. Moreover, the Magnus Ehrnrooth Foundation (Application No.12-9629-29) and RawMatters Finland Infrastructure (RAMI) and the Bioeconomy Facilities at Aalto University are also gratefully acknowledged.

Firstly, I would like to express my deepest and sincere gratitude to my supervisor Professor Marjatta Louhi-Kultanen. Thanks for offering me the precious opportunity to study at Aalto University, supplying valuable guidance and supporting my studies, as well as helping me to successfully apply for funding. Moreover, I appreciate that you respect and encourage my own thoughts and have given me a lot of freedom for my research. In every discussion with you, I always get suggestions, not commands. It has supported me to grow as a thoughtful and independent researcher.

I would like to thank my thesis advisor Prof. Daniel Lindberg for introducing me to the wonderland of thermodynamics. I am thankful to Dr. Bing Han for helping me to start my experimental research and for giving me valuable suggestions on my research progress. Many thanks to Prof. Zhihong Liu, Prof. Mari Lundström, Prof. Zhiyong Liu, Prof. Fupeng Liu, and Prof. Longgong Xia for their recommendations and encouragement regarding my studies. Further thanks go to all my co-authors in my research, especially Dr. Arshe Said and Prof. Rajabopathi Mani for their insightful discussions and valuable suggestions.

I would like to extend my thanks to my colleagues, Anna Zaykovskaya, Bernard Amano, Mitra Ila, Dr. Nahla Osmanbegovic, and David Sibarani for creating an excellent working atmosphere. Special thanks go to Seppo Jääskeläinen who helped me with designing and building all the experimental setups. I appreciate Dr. Juha-Pekka Pokki and Dr. Petri Uusi-Kyyny who helped me to work at the laboratory smoothly.

My special thanks go to my Chinese friends in Finland, especially Dr. Zulin Wang, Dr. Min Chen, Yuanmin Zou, Kezhou Song, Dr. Xingbang Wan, Tianxiang Nan, Siyu Zhou, and Prof. Fang Hu for their support and company during my doctoral studies.
Finally, I would like to express my warmest gratitude to my family, especially my parents, sister, brother-in-law, and niece. Thanks for your tremendous understanding and encouragement during my studies abroad. Without your support, it would not have been possible for me to undertake this journey.

Espoo, Finland, November 2023
Jianxin Zhang
张建鑫
Contents

Acknowledgements ............................................................................................................. 1
List of Abbreviations and Symbols .................................................................................... 5
List of Publications .............................................................................................................. 8
Author’s Contribution .......................................................................................................... 9
1. Introduction .................................................................................................................... 10
  1.1 Objective and scope ................................................................................................. 11
  1.2 Structure of the thesis .............................................................................................. 12
2. Research background ..................................................................................................... 13
  2.1 Cobalt extraction from primary resources ............................................................... 13
  2.2 Cobalt recovery from secondary resources ............................................................. 14
  2.3 Cobalt recovery from solutions via crystallization .................................................. 17
    2.3.1 Crystallizing cobalt sulfate from aqueous solutions ....................................... 17
    2.3.2 Cobalt carbonate precipitation from aqueous solutions ................................... 19
3. Experimental .................................................................................................................... 22
  3.1 Materials ................................................................................................................... 22
  3.2 Semi-batch vacuum evaporative crystallization ......................................................... 23
  3.3 Semi-batch carbonate precipitation .......................................................................... 24
  3.4 Batch cooling crystallization of CoSO₄ ................................................................. 24
    3.4.1 Solubility measurement ....................................................................................... 25
    3.4.2 MSZW and induction time determination ......................................................... 26
  3.5 Continuous cooling crystallization of CoSO₄ .............................................................. 27
  3.6 Analysis methods applied .......................................................................................... 28
    3.6.1 Analysis of solid samples .................................................................................. 28
    3.6.2 Analysis of liquid samples ................................................................................. 28
4. Results and discussion ...................................................................................................... 32
  4.1 Thermodynamics of CoSO₄ solution ............................................................................. 32
    4.1.1 Vapor pressure of CoSO₄ solution ....................................................................... 32
    4.1.2 Solubility of CoSO₄ in aqueous solutions ......................................................... 33
  4.2 Vacuum evaporative crystallization of CoSO₄ .............................................................. 34
4.3 Batch cooling crystallization of CoSO₄ ........................................... 36
4.3.1 Cooling rate and impurity effect on the CSD ......................... 37
4.3.2 Factors affecting the MSZW ..................................................... 37
4.3.3 Nucleation kinetics of CoSO₄ in pure solution from the MSZW 39
4.3.4 Factors affecting induction time ............................................ 41
4.4 Continuous cooling crystallization of CoSO₄ ............................ 44
4.4.1 Factors affecting product CSD ............................................. 44
4.4.2 Factors affecting kinetics ....................................................... 45
4.4.3 Models for kinetic rate estimation ........................................ 46
4.5 Hydrate forms of CoSO₄ and their dehydration in drying ...... 47
4.6 CoCO₃ precipitation ................................................................ 50
5. Summary ..................................................................................... 58
References ........................................................................................ 61
List of Abbreviations and Symbols

**Abbreviations:**

- AAS: Atomic Absorption Spectroscopy
- Abs: Absorbance
- CSD: Crystal Size Distribution
- C3DN: Classical 3D Nucleation
- DESs: Deep Eutectic Solvents
- EVs: Electric Vehicles
- E-NRTL: Electrolyte Non-Random Two-Liquid
- FBRM: Focused Beam Reflectance Measurement
- LIBs: Lithium-ion Batteries
- MSMPR: Mixed-Suspension, Mixed-Product-Removal
- MSZW: Metastable Zone Width
- PAR: Peak Area Ratio in Raman analysis
- PBEs: Population Balance Equations
- PXRD: X-ray Powder Diffraction
- SEM: Scanning Electron Microscope
- SCNL: Self-Consistent Nývlt-like
- TGA: Thermal Gravimetric Analysis
- UV-VIS: Ultraviolet–Visible

**Symbols**

- $A$: Pre-exponential factor, $#/m^3\cdot s$
- $B$: Thermodynamic parameter, -
\( B^o \) \hspace{1cm} \text{Nucleation rate, \#/m}^3\text{.s} \\
\( C \) \hspace{1cm} \text{CoSO}_4 \text{ solubility, mol/ kg water} \\
\( C_{\text{sat}} \) \hspace{1cm} \text{CoSO}_4 \text{ solubility at saturation temperature, mol/ kg water} \\
\( C_{\text{nucl}} \) \hspace{1cm} \text{CoSO}_4 \text{ solubility at nucleation temperature, mol/ kg water} \\
\( c \) \hspace{1cm} \text{CoSO}_4 \text{ concentration in the MSMPR mother liquor, g/mL} \\
\( c_0 \) \hspace{1cm} \text{CoSO}_4 \text{ concentration in the feeding solution, g/mL} \\
\( E_g \) \hspace{1cm} \text{Activation energy for growth, kJ/mol} \\
\( F \) \hspace{1cm} \text{Intercept in Classical 3D nucleation approach, -} \\
\( F_1 \) \hspace{1cm} \text{Slope in Classical 3D nucleation approach, -} \\
\( G \) \hspace{1cm} \text{Growth rate, \( \mu \)m/s} \\
\( J \) \hspace{1cm} \text{Nucleation rate, \#/m}^3\text{.s} \\
\( K \) \hspace{1cm} \text{Nucleation constant, \#/m}^3\text{.s} \\
\( k_B \) \hspace{1cm} \text{Boltzmann constant, } 1.380649 \times 10^{-23} \text{ J\cdot K}^{-1} \\
\( k_b \) \hspace{1cm} \text{Nucleation rate constant, -} \\
\( k_{g0} \) \hspace{1cm} \text{Growth rate constant, -} \\
\( k_v \) \hspace{1cm} \text{Volume based crystal shape factor, 0.471 (Octahedron)} \\
\( L \) \hspace{1cm} \text{Crystal size, \( \mu \)m} \\
\( L_{4,3} \) \hspace{1cm} \text{Mass weighted mean size, \( \mu \)m} \\
\( L_{i,av} \) \hspace{1cm} \text{Average crystal size of the i-th channel, \( \mu \)m} \\
\( m \) \hspace{1cm} \text{Molality, mol/kg solvent} \\
\( m \) \hspace{1cm} \text{Apparent order of nucleation in Eq. 4.1} \\
\( M_T \) \hspace{1cm} \text{Suspension density, kg/m}^3 \\
\( n \) \hspace{1cm} \text{Population density, \#/m}^3\cdot\text{\( \mu \)m} \\
\( n^o \) \hspace{1cm} \text{Nuclei population density, \#/m}^3\cdot\text{\( \mu \)m} \\
\( R \) \hspace{1cm} \text{Cooling rate, K/h} \\
\( R^2 \) \hspace{1cm} \text{Regression coefficient, -} \\
\( S \) \hspace{1cm} \text{Relative supersaturation, -} \\
\( T \) \hspace{1cm} \text{Solution temperature, K} \\
\( T_{\text{cry}} \) \hspace{1cm} \text{Crystallization temperature, K} \\
\( T_{\text{feed}} \) \hspace{1cm} \text{Saturated feeding temperature, K} \\
\( T_{\text{nucl}} \) \hspace{1cm} \text{Nucleation temperature of solution, K}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{sat}$</td>
<td>Temperature of saturation solution, K</td>
</tr>
<tr>
<td>$t_{ind}$</td>
<td>Induction time, min</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Slope in Eq.4.2, -</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Solid-liquid interfacial energy, J/m²</td>
</tr>
<tr>
<td>$\Delta C$</td>
<td>Supersaturation, g/g solvent</td>
</tr>
<tr>
<td>$\Delta L_i$</td>
<td>The width between the sizes channel $L_i$ to $L_{i+1}$, µm</td>
</tr>
<tr>
<td>$\Delta T_{max}$</td>
<td>Metastable zone width, K</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Density of crystal CoSO$_4$·7H$_2$O, 1.948 g/cm³</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Residence time, s</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Diameter, mm</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Intercept in Eq.4.2, -</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Molecular volume of CoSO$_4$·7H$_2$O, $2.396 \times 10^{-28}$ m³/mol</td>
</tr>
</tbody>
</table>
This doctoral dissertation consists of a summary and the following publications, which are referred to in the text by their numerals.


Author’s Contribution

Publication 1: ‘Semi-batch evaporative crystallization and drying of cobalt sulphate hydrates’

JZ designed the experimental setup and procedure, and conducted the evaporative crystallization experiments under the supervision of MLK, BH, and AS. JZ prepared the original draft and edited the manuscript based on the revisions and comments from MLK, BH, and AS. The particle size analysis was supervised by AS and BH.

Publication 2: ‘Process monitoring of cobalt carbonate precipitation by reactions between cobalt sulfate and sodium carbonate solutions to control product morphology and purity’

JZ developed the experimental procedure and conducted the cobalt carbonate precipitation experiments under the supervision of MLK. JZ prepared the original draft, and the final manuscript was revised, edited, and approved by MLK and RM. The Raman analysis and XRD analysis were supported by RM.

Publication 3: ‘Determination of nucleation kinetics of cobalt sulfate by measuring meta-stable zone width and induction time in pure and sulfuric acid solution’

JZ designed the experimental procedure and conducted the batch cooling crystallization experiments under the supervision of MLK. JZ modeled the nucleation kinetic data. JZ prepared the original draft and edited the manuscript based on the revisions and comments from MLK.

Publication 4: ‘Continuous cooling crystallization of cobalt sulfate from pure aqueous, H₂SO₄, and NiSO₄ solutions’

JZ designed the experimental procedure and conducted the continuous cooling crystallization experiments under the supervision of MLK. JZ modeled the kinetic data. JZ prepared the original draft and edited the manuscript based on the revisions and comments from MLK.
Climate change has been one of the major challenges of recent decades. To achieve greenhouse gas neutrality, the transportation and power sectors need to be restructured through electrification [1–3]. Cobalt (Co), which has been recognized as a critical raw material, plays a vital role in energy transition [4, 5]. Cobalt-based batteries, magnets, and superalloys are commonly used in electric vehicles (EVs), wind turbines, and other power generation technologies [6]. Beside the applications in the energy sector, cobalt is also widely applied in catalysts, ink, pigments, and as an additive for animal feed [7–10]. Of these, rechargeable batteries used in EVs, laptops, and mobile phones share the biggest demand for cobalt [11–13]. As the battery industry continues to develop dramatically, a strong growth in cobalt demand in the coming decades is expected by many researchers [14, 15].

With the fast-rising demand for cobalt, the cobalt supply chain is now also facing various risks [16]. The cobalt supply has a near-monopolistic supply structure, with the Democratic Republic of the Congo dominating the mining supply of cobalt with 74% in 2021, and China the biggest cobalt refiner providing 72% of total primary production [17–21]. Another fact is that over 80% of cobalt is mined as a byproduct of copper and nickel [22]. These factors may contribute to the rising uncertainties of global cobalt supply.

Nowadays, the cobalt supply comes from both primary minerals and recovery from secondary resources [23]. The traditional route for cobalt manufacture from primary minerals is a combination of pyrometallurgy and hydrometallurgy. In the pyrometallurgy process, the cobalt-containing matte, calcine, or alloy is produced by smelting or roasting. In the hydrometallurgical process, the cobalt-containing product from the pyrometallurgy process is leached by acidic or basic solutions. The cobalt product is obtained from the purified leachate via electrowinning, precipitation, or crystallization.

Since the primary mineral supply of cobalt faces risks from Ni and Cu mining work and uneven geographical distribution, the sustainable recovery of Co from secondary resources has now become timely. The secondary resources of Co include the slags from some metallurgical processes, waste catalysts, magnets,
superalloys, and waste batteries. Among these cobalt secondary resources, waste batteries containing cobalt show the greatest recycling opportunities in battery industry. Due to its high selectivity and environment friendliness, hydrometallurgy has widely been applied for recycling Co from waste batteries. As part of the cobalt production, recovering cobalt from leachate is an important process, whether for primary or secondary resources.

There are two main conventional methods for recovering cobalt from cobalt-containing solutions. One method is electrowinning, which involves the use of an electrical current to deposit cobalt metal. Another method is crystallization or precipitation, which allows for the formation of cobalt salts. Due to the high energy consumption of electrowinning and wide application of cobalt salts, the crystallization of cobalt is attracting interest from cobalt manufacturers and researchers [24]. In industry, crystallizing cobalt sulfate via cooling or evaporative crystallization, and precipitating cobalt hydroxide or carbonate are applied in some companies. Concerning laboratory studies, results on antisolvent crystallization of cobalt sulfate have been reported by Aktas et al. [25], Peng et al. [26] and Zheng et al. [27] have investigated the precipitation of cobalt carbonate, and Djoudi et al. [28] have studied the precipitation of cobalt hydrate for cobalt recycling from waste lithium batteries. However, only a few research studies have reported these processes in a detailed manner. Operating conditions such as temperature, mixing, impurities, etc., have a great effect on the crystallization process and product properties. Moreover, theoretical studies such as kinetics and thermodynamics are vital for designing a crystallization process. To achieve cobalt recovery in an effective and sustainable manner, this dissertation work can deliver a deeper understanding of the crystallization of cobalt salts in both batch and continuous processes through comprehensive experimental and theoretical studies.

1.1 Objective and scope

In the work for the present thesis, the recovery of cobalt salts from aqueous cobalt sulfate solutions using semi-batch vacuum evaporative crystallization, batch and continuous cooling crystallization, and carbonate precipitation, has been investigated comprehensively. The main objectives of this thesis work are:

1: To investigate the influence of crystallization and drying temperatures and the heating power used in crystallization on crystalline product properties in vacuum evaporative crystallization.

2: To understand the cobalt carbonate precipitation mechanisms by monitoring the process and to evaluate the factors affecting precipitation for cobalt recovery from aqueous solutions.
3: To explore batch cooling crystallization for cobalt sulfate and determine the nucleation kinetics via metastable zone width (MSZW) and induction time approaches.
4: To investigate continuous cooling crystallization for cobalt sulfate in an MSMPR crystallizer and build kinetic models for nucleation and growth rates.

An overview of the crystallization methods for cobalt salts investigated in this thesis work is described schematically in Figure 1.1. The links between the research topics of the thesis to the objectives and Publications 1-4 are also shown. The detailed results can be found in Publications 1-4 as well as in this thesis.

Figure 1.1. Schematic diagram of the thesis research work and its interconnections.

1.2 Structure of the thesis

The thesis consists of three scientific peer-reviewed journal articles (Publications 1-3) and one submitted manuscript (Publication 4) which are attached to the thesis. The thesis is structured as follows: Chapter 1 is a brief introduction of the thesis work, Chapter 2 introduces the relevant research background, Chapter 3 presents the experimental details, while Chapter 4 illustrates the main results with a detailed discussion. In Chapter 5, the main findings of the whole doctoral thesis are summarized and considerations for future work are provided.
2. Research background

In this chapter, a detailed summary of cobalt resources and the most common treatment technologies are introduced. Crystallization as one of the key unit operations has been widely employed for the separation, purification, and production of cobalt salts. The feasible crystallization methods including evaporative, cooling, and reactive crystallization are presented.

2.1 Cobalt extraction from primary resources

Cobalt is not a rare element, with a concentration of 0.0023 % in the Earth’s crust, but its geographical distribution is highly uneven in that over 50 % cobalt is mined in the Democratic Republic of the Congo [29]. Primary cobalt minerals are always found in combination with nickel or copper, and can be divided into the following five categories: Co-containing Cu-Ni sulfide mineral, Cu-Co concentrate, arsenic cobalt concentrate, nickel laterite, and cobalt pyrite concentrate [30, 31]. Cobalt extraction from primary resources is normally a combination of a pyrometallurgical process and a hydrometallurgical process [32, 33]. A comprehensive summary of the extraction routes is shown in Figure 2.1.

In the pyrometallurgical process, various pyrometallurgical technologies are applied for different cobalt concentrates. For arsenic cobalt concentrate, a cobalt-containing calcine is obtained after smelting and oxidation roasting [34]. Combined smelting and blowing is applied for the treatment of cobalt-containing Cu-Ni sulfide mineral [35]. Cobalt matte is generated from the converter slag and a cobalt-bearing filter cake is collected after Ni electrolysis. To treat Cu-Co concentrate, smelting and sulfating roasting are applied for oxidized and sulfide ore, to produce a Co-Cu alloy and calcine, respectively [36–39]. Oxidation roasting and reduction roasting are adopted for cobalt extraction from cobalt pyrite concentrate and nickel laterite, respectively [40–44]. The products from all the processes mentioned above, i.e., cobalt matte, cobalt-containing filter cake, and calcine, need to be further refined by a hydrometallurgical process.

The hydrometallurgical process for cobalt extraction from primary resources consists mainly of leaching, purification, and production. In the leaching stage,
an acid such as sulfuric acid, hydrochloric acid, or nitric acid can be applied since cobalt is soluble in acid solutions [45–47]. Of the acids mentioned above, sulfuric acid is the most popular leaching reagent. In some processes for Co-Ni sulfide and nickel laterite, ammonia solution pressure leaching can be applied [48–50]. After leaching, cobalt is dissolved into the solution, and other impurities such as Cu, Ni, Fe, etc. are also dissolved simultaneously. Before cobalt production from the leachate, a purification process is mandatory. Solvent exchange and selective precipitation are the most common techniques for leachate purification to remove impurities such as Ni, Fe, and Cu [51–55]. The purified leachate is then routed to cobalt production. Cobalt can be produced as cobalt metal by electrowinning, as cobalt metal powder by hydrogen reduction, or as cobalt salts by crystallization [56–59].

Moreover, with the grade of ores decreasing, the application of heap leaching to recover valuable metals from low-grade ores, such as Cu, Ni, and Co, is continuously increasing [60, 61]. In the heap leaching process, the valuable metals are extracted directly from crushed ores. The metal-containing leachate is sent to metal production after purification, which is similar to the hydrometallurgical process mentioned above. The agents for heap leaching can be acidic or basic solutions, and bacteria or fungi-based bio leaching solutions [62–64].

2.2 Cobalt recovery from secondary resources

Given the uncertainties and risks associated with the primary cobalt supply, exploring secondary resources can be a viable solution for ensuring a stable and sustainable cobalt supply in the future. Secondary cobalt resources include the slag and sludge generated in Ni, Cu, and Zn refineries, flotation tailings, cobalt-based alloy scrap, waste batteries, and catalysts [65–69].

The technologies for cobalt recovery from secondary resources can be classified into four main routes: pyrometallurgical route, hydrometallurgical route, pyro-hydrometallurgical route, and bio-hydrometallurgical route [23, 70, 71]. For cobalt-bearing slag and sludge from a metallurgical process, the pyro-hydrometallurgical route is widely applied. The hydrometallurgical route, pyrometallurgical and combination of both routes are quite similar to the conventional route for primary minerals, as shown in Figure 2.1. In the purification process, selective precipitation and solvent exchange are often applied. In an earlier study, the author investigated the removal of Al and Fe by phosphate and hydroxide precipitation, and Ni separation by solvent extraction in the waste lithium-ion batteries (LIBs) recovery process [72]. The pre-treatment techniques and reagents for leaching are selected based on the cobalt concentration and the prop-
Research background

properties of the secondary resources. Besides the conventional acidic or basic leaching reagents, deep eutectic solvents (DESs) are a promising alternative for recycling waste LIBs, since DESs have a high capacity for dissolving metal oxides, and are often low-cost and easily obtained [73]. Various DES systems were studied for metals recovery from waste LIBs. With DES leaching, Co recovery efficiency can approach 100% [74]. Some researchers have also investigated the direct repair of waste LIBs with DESs [75]. The bio-hydrometallurgical route, which uses bacteria-based or fungi-based leaching, is a new trend due to its low cost and low energy consumption, and environment friendliness. However, the disadvantages of the bio-hydrometallurgical route are also significant in that the leaching efficiency is low, and process control is difficult [76–79].

To sum up, although some cobalt alloys can be obtained directly from the pyrometallurgical process, most cobalt products such as cobalt metal and salts are generated from cobalt-containing solutions. Crystallization could play an important role in recovering cobalt from such solutions.
Figure 2.1 Extraction routes for cobalt extraction from primary resources [80, 81].
2.3 Cobalt recovery from solutions via crystallization

Regarding the routes for cobalt extraction, cobalt sulfate solution is one of the most common streams since sulfuric acid is widely used in both leaching and leachate purification (i.e., solvent extraction) [82–84]. Recycling cobalt from sulfate solutions as cobalt salts can be realized using crystallization methods. The most common cobalt salts obtained by crystallization include cobalt sulfate, cobalt carbonate and cobalt hydroxide. In this thesis, cobalt sulfate and cobalt carbonate were selected as the target components.

2.3.1 Crystallizing cobalt sulfate from aqueous solutions

Cobalt sulfate is one of the most common cobalt salts and has been widely applied in the glass industry as a pigment, in animal fodder as an additive, and in battery industries as a cobalt source. For controlling and optimizing crystallization processes, and producing CoSO$_4$ with desired properties, a good understanding on crystallization thermodynamics and kinetics is essential.

2.3.2 Thermodynamics for cobalt sulfate system

Thermodynamics on the solubility and phase diagrams plays a crucial role in the selection of crystallization methods, the state of products, and yield prediction.

Cobalt sulfate exists in three hydrate forms: heptahydrate, hexahydrate, and monohydrate. The solubilities at various temperatures shown in Table 2.1, indicate that CoSO$_4$ crystallization can be achieved with a relatively good yield by evaporating water. Additionally, as the solubility of CoSO$_4$ in water decreases with temperature, cooling crystallization could also be applied for CoSO$_4$ production.

Based on experimentally measured solubilities, thermodynamic models for the CoSO$_4$-H$_2$O binary system have been developed to calculate solution properties and predict phase equilibria. Vielma [85] investigated the Pitzer model for CoSO$_4$ at temperatures between 270 to 374 K under atmospheric pressure. Iliuta et al. [86] modeled cobalt sulfate solubility using the extended UNIQUAC model. According to Vielma, CoSO$_4$·7H$_2$O is stable at temperatures below 45 °C, CoSO$_4$·6H$_2$O is stable at temperatures between 45 to 64 °C, and CoSO$_4$·H$_2$O is stable at temperatures higher than 64 °C. Moreover, the yield for CoSO$_4$ from a pure solution can be estimated based on the phase diagram. Although the thermodynamics for a pure CoSO$_4$ aqueous solution has been investigated by many researchers, studies on solutions containing impurities are limited.

Ma et al. [87] investigated the eutectic freeze crystallization of CoSO$_4$ from both pure aqueous and dilute sulfuric acid solutions. They presented phase diagrams for CoSO$_4$-H$_2$O and CoSO$_4$-0.5 m H$_2$SO$_4$-H$_2$O, in temperature range between the eutectic point and 20 °C. The phase diagrams revealed that with 0.5 m H$_2$SO$_4$,
the solubility of CoSO$_4$ decreased significantly. Furthermore, the eutectic point shifted from 18.7 wt% at -2.6 °C to 13.4 wt% at -5.4 °C.

In this thesis, sulfuric acid and nickel sulfate have been selected as critical impurities, since these two compounds commonly exist in the cobalt manufacturing process. The solubility of CoSO$_4$ in water with different H$_2$SO$_4$ and NiSO$_4$ concentrations has been measured, and the effects of these impurities on the stable hydrates have also been investigated.

Table 2.1 Cobalt sulfate solubility in water at various temperatures (mol/kg water).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mullin [89]</td>
<td>1.645</td>
<td>1.935</td>
<td>2.335</td>
<td>/</td>
<td>2.697</td>
<td>3.097</td>
<td>/</td>
<td>3.871</td>
<td>4.156</td>
</tr>
<tr>
<td>Stable form</td>
<td>7H</td>
<td>7H</td>
<td>7H</td>
<td>7H</td>
<td>7H</td>
<td>6H</td>
<td>6H</td>
<td>1H</td>
<td></td>
</tr>
</tbody>
</table>

Note: 7H, 6H, and 1H refer to heptahydrate, hexahydrate, and monohydrate, respectively.

2.3.2.1 Kinetics for cobalt sulfate crystallization

Crystallization kinetics is conventionally characterized in terms of the rates of nucleation and growth. These rates are affected by impurities and operating conditions such as temperature and mixing performance. The crystallization kinetics essentially governs the crystal size, morphology, and purities of the final product.

Nucleation, the starting points for crystal growth, involves the creation of small clusters of solute molecules. There are two mechanisms for the nucleation which are primary nucleation and secondary nucleation. Primary nucleation refers to the formation of new crystals which is the initial step in the crystallization process without the influence of existing crystals. Secondary nucleation refers the birth of new crystals in the presence of parent crystals of the same substance which occurs after primary nucleation and is influenced by the presence of already formed crystals. Both primary and secondary nucleation have critical effects on crystal size, purity, and yield of final product. For CoSO$_4$, however, no previous studies have reported the cooling crystallization kinetics.
To determine the primary nucleation kinetics of CoSO$_4$ cooling crystallization, theoretical models and experimental data collected from non-isothermal MSZW measurements and isothermal induction time measurements were used. Calculating nucleation kinetics from MSZW data, Self-consistent Nývlt-like approach (SCNL) and classical 3D nucleation approach (C3DN) were adopted. For nucleation kinetics calculation from induction time, classical nucleation theory was applied with the assumption that the induction is inversely proportional to the nucleation rate. The detailed calculations about primary nucleation kinetic are shown in Sections 4.3.3 and 4.3.4.

Moreover, the secondary nucleation and growth rates were studied with the continuous crystallization which is carried out in a Mixed-Suspension, Mixed-Product-Removal crystallizer (MSMPR). The secondary nucleation kinetics and the growth rate of CoSO$_4$ were determined based on the crystal size distribution (CSD) at steady state and population balance equations (PBEs). The calculations and obtained results are shown in Sections 4.4.2 and 4.4.3, and Publication 4.

### 2.3.3 Cobalt carbonate precipitation from aqueous solutions

Precipitation refers to the process where a dissolved substance in a solution transforms into a solid phase under the high supersaturation. Reactive precipitation method, where a poorly soluble precipitate is formed by chemical reactions between the reactants, has been applied in this thesis. Since cobalt carbonate is sparingly soluble in water, it can be produced with the carbonate or bicarbonate precipitation process. Cobalt carbonate is an important salt which can be used as a pigment, catalyst, or cobalt source for batteries [91–94]. In the precursor field, industrial-scale cobalt carbonate precipitation has been successfully performed to produce the cobalt oxide that is used in a lithium battery [82, 83]. Moreover, precipitation from CoCl$_2$ or Co(NO$_3$)$_2$ (raw materials) and NH$_4$HCO$_3$ (precipitator) solutions has been widely studied, whereas only a few studies have focused on CoSO$_4$ as a cobalt source [97–100]. Regarding the reactive crystallization of CoCO$_3$ from sulfate solution, Peng et al. [26] proposed a two-step process. In their study, cobalt was first precipitated as Co$_2$CO$_3$(OH)$_2$ using NH$_4$HCO$_3$ as the precipitator. CoCO$_3$ product is then obtained after hydrothermal treatment at temperatures of 125-150 °C.

Although CoCO$_3$ precipitation has been widely investigated, there are very few studies in the literature reporting the use of CoSO$_4$ and Na$_2$CO$_3$ as raw materials and their impact on CoCO$_3$ precipitation. Furthermore, carbonate precipitation is a complex process where the dissociation of carbonate species and hydrolysis reactions can vary greatly at different pHs. In the CoCO$_3$ precipitation, the possible occurred reactions are listed in Table 2.2 and the reaction constant values in Table S1 as supplementary data in Publication 2. An E-pH diagram of Co-C-
H$_2$O system is drawn by HSC 10 software as shown in Figure 2.2. The diagram shows the stable zone for cobalt species. Cobalt hydroxide is stable at pH higher than 10 and cobalt carbonate is stable at lower pH (3-10), and the stable zones for both two solids shift to lower pH with a temperature increase. The anions species and its concentration, and precipitate properties, which affecting by precipitation conditions, are important to ensure the required properties of the final product. In Publication 2, CoCO$_3$ precipitation using CoSO$_4$ and Na$_2$CO$_3$ as reactants was investigated under various operating conditions. The precipitation mechanism was studied using online and offline measurements.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na$_2$CO$_3$ → 2Na$^+$ + CO$_3^{2-}$</td>
</tr>
<tr>
<td>2</td>
<td>CO$_3^{2-}$ + H$_2$O ⇋ HCO$_3^-$ + OH$^-$</td>
</tr>
<tr>
<td>3</td>
<td>OH$^-$ + H$^+$ ⇋ H$_2$O</td>
</tr>
<tr>
<td>4</td>
<td>CO$_3^{2-}$ + H$^+$ ⇋ HCO$_3^-$</td>
</tr>
<tr>
<td>5</td>
<td>HCO$_3^-$ + H$^+$ → H$_2$CO$_3$</td>
</tr>
<tr>
<td>6</td>
<td>H$_2$CO$_3$ → H$_2$O + CO$_2$ (g)</td>
</tr>
<tr>
<td>7</td>
<td>HCO$_3^-$ → CO$_2$ (g) + OH$^-$</td>
</tr>
<tr>
<td>8</td>
<td>Co$^{2+}$ + CO$_3^{2-}$ → CoCO$_3$ (s)</td>
</tr>
<tr>
<td>9</td>
<td>2Co$^{2+}$ + CO$_3^{2-}$ + 2OH$^-$ → Co$_2$(CO$_3$)(OH)$_2$(s)</td>
</tr>
<tr>
<td>10</td>
<td>Co$^{2+}$ + 2OH$^-$ → Co(OH)$_2$(s)</td>
</tr>
</tbody>
</table>
Figure 2.2 E-pH diagram for Co-C-H₂O system with ionic concentration of 1 mol/L and temperature of 40 to 65 °C.
3. Experimental

In this chapter, a detailed explanation of the experimental methods employed in this thesis is provided. It includes the information of the chemicals utilized, different crystallization setups and processes, and characterization methods applied for crystal and mother liquor samples.

3.1 Materials

In this thesis, synthetic CoSO₄ solution was used as the cobalt resource for all the crystallization processes. The synthetic CoSO₄ solutions were prepared by dissolving commercial cobalt sulfate heptahydrate in water at a specific concentration. H₂SO₄ was used to adjust the pH in Publication 2. Na₂CO₃ solution, prepared by dissolving Na₂CO₃ in water, was used as a reactant in the cobalt carbonate precipitation study (Publication 2). The main impurities were H₂SO₄ (Publications 3 and 4) and NiSO₄ (Publication 4). All of the chemicals mentioned above are listed in Table 3.1, along with their purities and suppliers. Deionized water was used for preparing all of the solutions.

Table 3.1 Chemicals and their purities and suppliers.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Purity /wt.%</th>
<th>Supplier</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄·7H₂O</td>
<td>≥ 99</td>
<td>Sigma-Aldrich Inc.</td>
<td>1, 3, 4</td>
</tr>
<tr>
<td>CoSO₄·7H₂O</td>
<td>≥ 99</td>
<td>Acros Organics</td>
<td>2</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>≥ 99</td>
<td>Acros Organics</td>
<td>2</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>≥ 95</td>
<td>VWR Chemicals</td>
<td>2</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>≥ 98</td>
<td>Sigma-Aldrich Inc.</td>
<td>3, 4</td>
</tr>
<tr>
<td>NiSO₄·7H₂O</td>
<td>≥ 99</td>
<td>Sigma-Aldrich Inc.</td>
<td>4</td>
</tr>
</tbody>
</table>

The initial compositions for the synthetic solutions were varied for different crystallization processes. In the study on evaporative crystallization (Publication 1), CoSO₄ solutions of slightly reduced concentrations compared with their solubilities at various temperatures were prepared. For carbonate precipitation
Experimental

(Publication 2), 2 mol CoSO\(_4\)/kg water solutions with various H\(_2\)SO\(_4\) concentrations were utilized as the cobalt resource and 1 mol Na\(_2\)CO\(_3\)/kg water solution was applied as reactant. For batch and continuous cooling crystallization (Publications 3 and 4), saturated solutions with various impurities (H\(_2\)SO\(_4\), NiSO\(_4\)) at different temperatures were prepared based on the measured solubility.

3.2 Semi-batch vacuum evaporative crystallization

The evaporative crystallization experiments were conducted in a vacuum system developed in the thesis work, as depicted in Figure 3.1. A 400 mL glass reactor, equipped with a four-pitched-blade turbine and baffles, was used as the crystallizer in an EasyMax 402 system (Mettler Toledo). A vacuum pump (MPC 301Z), along with a valve and pressure sensor (WIKA, A-10), was employed for vacuum pressure control and monitoring. The evaporated water was collected in a distilling receiver (Anschütz-Thiele, 50 mL) after condensation in a Liebig condenser. This study aimed to investigate the effects of crystallization temperature, heating power, and mixing on the product properties. Four different crystallization temperatures (30, 40, 60 and 80 °C) were investigated. The temperature was controlled by adjusting the vacuum pressure to maintain the solution at its boiling point. The heating power was varied by changing the temperature difference between the heating jacket and the solution. The vacuum evaporation process took 30 minutes from the start of solution boiling. After evaporation, a 30-minute aging period was maintained with a constant solution temperature (same as the evaporative process) but at atmospheric pressure.

![Figure 3.1 Setup of semi-batch evaporative crystallization. (Adapted with permission from Publication 1. Copyright 2022 the authors, published by Elsevier.)](image-url)
3.3 Semi-batch carbonate precipitation

The carbonate precipitation experiments were conducted in a 400 mL glass reactor equipped with baffles and a pitched-blade turbine with four blades (Φ=38 mm). The temperature and mixing speed were controlled using iControl software. The pH value was continuously monitored throughout the precipitation process, and the final pH was adjusted by varying the concentration of sulfuric acid in the initial $\text{CoSO}_4$ solution. Focused beam reflectance measurement (FBRM, Particle track G400, Mettler Toledo) was employed to monitor the precipitation. In the experiment, 100 g $\text{CoSO}_4$ solution (2 $m$) was continuously added to a 200 g $\text{Na}_2\text{CO}_3$ solution (1 $m$) at different reactant addition times. After the addition of reactant solution was complete, an aging period was introduced to ensure complete precipitation. The suspension was then filtered, and the precipitates were further analyzed after being washed twice with rinsing 100 mL hot deionized water and dried at 60 °C. The mother liquor was collected for chemical analyses. In order to explore the precipitation mechanism, slurry samples were collected at various pH values over the precipitation period. After filtration, both the mother liquor and filtered precipitates were subjected to chemical analysis, and solid phase analysis was also carried out on the precipitated samples. A diagram of the experimental setup is shown in Figure 3.2.

![Diagram of the experimental setup for carbonate precipitation.](image)

Figure 3.2 Experimental setup for carbonate precipitation. (Reprinted with permission from Publication 2. Copyright 2023 the authors, published by Elsevier.)

3.4 Batch cooling crystallization of $\text{CoSO}_4$

The batch cooling crystallization experiments were conducted in a 100 mL glass reactor equipped with a four-pitched-blade turbine stirrer. Temperature control was achieved using iControl software, which had a temperature measurement
Experimental accuracy of ± 0.01 K. To detect nucleation and monitor the variation in crystal number during the cooling crystallization, FBRM was employed. The experimental setup is illustrated in Figure 3.3. For the experiment, saturated CoSO$_4$ solutions at 303.15 K with different H$_2$SO$_4$ concentrations (0, 0.2, 0.4, and 0.6 m) were prepared. The solution was initially heated to 308.15 K and held there for 30 minutes to ensure the absence of particles. Subsequently, the solution was cooled down to 283.15 K at various cooling rates (3, 6, and 12 K/h). Finally, a 30-minute aging time was applied. After filtration and washing, solid samples were collected for further analysis. The solubility of CoSO$_4$ with different H$_2$SO$_4$ concentrations was measured in the batch cooling crystallization, and the nucleation kinetics were investigated by measuring the MSZW and induction time.

![Figure 3.3 Setup for batch cooling crystallization. (Reprinted with permission from Publication 2. Copyright 2023 the authors, published by Elsevier.)](image)

### 3.4.1 Solubility measurement

The solubilities of CoSO$_4$ at various temperatures were determined using the isothermal method, with different concentrations of H$_2$SO$_4$ (0, 0.1, 0.2, 0.4, 0.6 m, Publication 3) or NiSO$_4$ (0, 0.2, 0.3, 0.4 m, Publication 4). To ensure preparation of a saturated solution, an excess of solid CoSO$_4$·7H$_2$O was added and dissolved in a solution with specific concentrations of impurities (H$_2$SO$_4$, NiSO$_4$). The resulting suspensions were then stirred at the desired temperature for 48 hours to reach equilibrium. After filtration, the solution samples were used to measure the concentrations of Co and impurities (NiSO$_4$, H$_2$SO$_4$). The concentration measurement details are explained below in Section 3.6.2. The final solubility data was calculated as the average value from three parallel experiments for each condition.
3.4.2 MSZW and induction time determination

The conventional polythermal method, as described by Mullin [89], was used to measure the MSZW of CoSO\(_4\) cooling crystallized from aqueous solution with varying H\(_2\)SO\(_4\) concentrations. The detailed process is as follows: (1) A saturated CoSO\(_4\) solution with a specific amount of H\(_2\)SO\(_4\) was prepared at the saturation temperature; (2) The solution, when heated to a temperature surpassing the saturation temperature by 5 K, was subjected to a 30-minute holding period to verify the absence of any particles within the solution; (3) Subsequently, the solution was left to cool down at different rates (3, 6, 9, 12, 15 K-h\(^{-1}\)). Figure 3.4(a) shows that the particle counts detected by FBRM and the change in solution temperature were used to identify nucleation. The temperature at the point of nucleation was recorded as \(T_{\text{nucl}}\). The difference between the \(T_{\text{sat}}\) (temperature at which the solution is saturated with CoSO\(_4\)) and \(T_{\text{nucl}}\) was recorded as the MSZW (\(\Delta T_{\text{max}}\)), which can be calculated using Equation 3.1:

\[
\Delta T_{\text{max}} = T_{\text{sat}} - T_{\text{nucl}}
\]  

(3.1)

For induction time measurements, the isothermal measurement method was applied, as shown in Figure 3.4(b). The first two steps for induction time measurement are the same as the steps for measuring the MSZW. In the next step, unlike the step in the MSZW procedure, the clean saturated solution was cooled to the target \(T_{\text{nucl}}\) as fast as possible and then the solution was kept at \(T_{\text{nucl}}\) until nucleation occurred. Nucleation was determined by FBRM and the temperature reaction. The period from attaining \(T_{\text{nucl}}\) to the observation of nucleation was recorded as the induction time (\(t_{\text{ind}}\)). In order to ensure accuracy, three parallel experiments were conducted for both MSZW and induction time measurements.

Figure 3.4 Measuring strategy for: (a) MSZW and (b) induction time. (Reprinted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)
3.5 Continuous cooling crystallization of CoSO₄

The continuous cooling crystallization of CoSO₄ was performed using the MSMPR setup, as shown in Figure 3.5. A 500 mL jacketed reactor connected to a thermostat (Lauda ECO RE630) was used as the crystallizer. A pitched-blade turbine was used for mixing and four baffles were used to improve mixing. The feed solution, contained in a 3 L glass container, was mixed and maintained at a temperature 5 °C higher than the saturation temperature using a magnetic stirrer with heating. Two peristaltic pumps (Masterflex, L/S) equipped with different tube sizes were used for feeding (tube L/S 16, 3.1 mm) and product removal (tube L/S 18, 7.9 mm). FBRM was employed to identify the steady state.

![Diagram](image)

Figure 3.5 Schematic diagram of the MSMPR setup.

The experimental procedure was as follows: (1) A 300 mL saturated CoSO₄ solution was placed in a crystallizer and rapidly cooled to $T_{cry}$. (2) The feed solution was continuously pumped into the crystallizer at a specified feeding rate, while the product slurry was intermittently removed for 10 seconds each minute. (3) Once steady state was achieved, suspension samples were taken for filtration. The steady state was confirmed using FBRM. After filtration, solid samples were collected for CSD and morphology analysis. The mother liquor was used for suspension density and supersaturation measurements. This study aimed to investigate the effects of supersaturation (adjusted by residence time through the feeding rate), suspension density (temperature difference between feed and crystallization), crystallization temperature, mixing, and impurities (NiSO₄, H₂SO₄).
3.6 Analysis methods applied

3.6.1 Analysis of solid samples

The CSD for solid samples obtained from experiments was analyzed by a wet method using a particle size analyzer (Malvern Master Sizer 2000) equipped with a dispersion unit (Hydro 2000 SM). The sample dispersant was ethanol (99.5%, VWR) for CoSO$_4$ (Publications 1, 3, and 4) and deionized water for CoCO$_3$ (Publication 2). The phases of the solid samples were identified by X-ray powder diffraction (PXRD; X’Pert PRO; Cu, $\lambda$K$_{\alpha 1}$=1.5406 Å) operated at 40 kV and 40 mA (Publications 1-3). The morphology of the solid samples was observed using a TESCAN MIRA3 SEM (Publications 1 and 2) and an Olympus BX53M optical microscope (Publications 3 and 4). TGA (thermal gravimetric analysis, Q 500, TA instruments) measurement and a Raman spectrometer (inVia™ confocal Raman microscope, Renishaw) were utilized to identify the hydrate forms of CoSO$_4$ in Publications 1 and 3. The concentration of Co and Na in the product obtained from carbonate precipitation was determined by AAS (Atomic Absorption Spectroscopy, Varian AA240) after dissolving the product into a mixture of nitric acid and hydrochloric acid.

3.6.2 Analysis of liquid samples

For liquid samples, the concentrations of Co and Ni were measured using a UV-VIS spectrophotometer (HACH, DR 6000) with the calibration models detailed in Section 3.6.2.1 below. The concentrations of SO$_4^{2-}$, CO$_3^{2-}$, and HCO$_3^{-}$ were determined with a Raman spectrometer (Renishaw inVia™) using the calibration models shown in Section 3.6.2.2. Furthermore, to transfer the concentration units between volume and mass based, the density of the liquid sample at specific temperatures was determined with a density meter (DMA 5000M, Anton Paar).

3.6.2.1 UV-VIS measurement for Co and Ni concentration

In UV-VIS measurement, there is a proportional relationship between the light absorbance with molecular concentration, molar absorptivity, and the path length of light through the sample. The concentration of Co and Ni was determined by building the calibration model for the absorbance of peaks at 512 nm for Co and 395 nm for Ni against concentration [101–103]. In this thesis, the UV-VIS measurements were conducted using a quartz cuvette with a path length of 10 mm. The scan range of the measurements was set to between 200 and 900 nm, with a scan speed of 240 nm/min. An average value for each sample was obtained after three parallel measurements. In Publication 3, the calibration model for Co concentration was built by measuring the absorbance of the Co standard solution with a concentration range of 0.01 to 0.05 M, as shown
in Figure 3.6(a)(b). Based on the linear fitting shown in Figure 3.6(b), the Co concentration could be determined by Equation 3.2:

\[
C(\text{Co, mol/L}) = 0.204 \times \text{Abs}_{512} - 0.004 \quad R^2 = 0.999 \quad (3.2)
\]

In Publication 4, where the impurity NiSO\textsubscript{4} was considered, new calibration models for Co and Ni concentration were built by measuring the absorbance of pure Co standard solutions and mixed Co-Ni standard solutions. The spectra and linear fitting of concentration against absorbance are displayed in Figures 3.6(c) and (d). Figure 3.6(c) shows that the effect of Ni on Co absorbance can be ignored when the Ni concentration is in the range of 0-10 g/L. The Co concentration can be determined by Equation 3.3. Moreover, there is an overlapping between the peak of Ni at 395 nm and peak of Co at 512 nm, meaning that both Co and Ni can contribute to the absorbance of the peak at 395 nm. The absorbance at 395 nm contributed by Co can be estimated by Equation 3.4. The net absorbance at 395 nm for Ni can be calculated by Equation 3.5. The Ni concentration can be determined by Equation 3.6.

\[
C(\text{Co, g/L}) = 12.549 \times \text{Abs}_{512} - 0.742 \quad R^2 = 0.999 \quad (3.3)
\]
\[
\text{Abs}_{395,\text{Co}} = 0.0048 \times C(\text{Co, g/L}) + 0.0574 \quad R^2 = 0.998 \quad (3.4)
\]
\[
\text{Abs}_{395,\text{Ni}} = \text{Abs}_{395} - \text{Abs}_{395,\text{Co}} \quad (3.5)
\]
\[
C(\text{Ni, g/L}) = 11.733 \times \text{Abs}_{395,\text{Ni}} + 0.045 \quad R^2 = 0.999 \quad (3.6)
\]

3.6.2.2 Raman measurement for SO\textsubscript{4}\textsuperscript{2-}, CO\textsubscript{3}\textsuperscript{2-}, and HCO\textsubscript{3} concentrations

The intensity of Raman signals exhibits a direct correlation with the concentration of the corresponding molecules [104]. A calibration model, established based on the relationship between the Raman spectral intensity and solute concentration, enabled the determination of solute concentration. It is important to note that the Raman spectral intensity can be influenced by measurement conditions and laser power stability. To minimize these influences, the water band at 1643 cm\textsuperscript{-1} was selected as the internal standard in this thesis [105]. In Publication 2, the calibration models for measuring SO\textsubscript{4}\textsuperscript{2-}, HCO\textsubscript{3}\textsuperscript{-}, and CO\textsubscript{3}\textsuperscript{2-} concentrations were constructed by linear fitting between SO\textsubscript{4}\textsuperscript{2-}, HCO\textsubscript{3}\textsuperscript{-}, and CO\textsubscript{3}\textsuperscript{2-} concentrations with the area ratio of the peak at 980 cm\textsuperscript{-1}, 1015 cm\textsuperscript{-1}, and 1066 cm\textsuperscript{-1}, respectively, divided by the peak of the water bond (1643 cm\textsuperscript{-1}), as shown in Figure 3.7(d) [93, 94]. The Raman spectra for SO\textsubscript{4}\textsuperscript{2-}, HCO\textsubscript{3}\textsuperscript{-}, and CO\textsubscript{3}\textsuperscript{2-} with various concentrations are also shown in Figures 3.7(a), (b), and (c), respectively. The concentration for SO\textsubscript{4}\textsuperscript{2-}, HCO\textsubscript{3}\textsuperscript{-}, and CO\textsubscript{3}\textsuperscript{2-} can be calculated using Equations 3.7, 3.8, and 3.9, respectively.
Experimental

\[ C(SO_4^{2-}, \text{molality}) = 0.3615 \times PAR_{980/1640} - 0.0128 \quad R^2 = 0.999 \quad (3.7) \]

\[ C(HCO_3^-, \text{molality}) = 1.5249 \times PAR_{1015/1640} - 0.0244 \quad R^2 = 0.999 \quad (3.8) \]

\[ C(CO_3^{2-}, \text{molality}) = 0.7912 \times PAR_{1066/1640} + 0.0420 \quad R^2 = 0.996 \quad (3.9) \]

Figure 3.6 Calibration models for ionic concentrations: (a) UV-VIS spectra of cobalt standard solutions; (b) relationship between Abs. of peaks at 512 nm and Co concentration; (c) UV-VIS spectra of standard pure Co solutions and mixing solutions of Co and Ni; (d) relationships between Abs. of peaks at 512 nm and Co concentration, and Net Abs. of peaks at 395 nm contributed by Ni concentration. (Adapted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)
Figure 3.7. Raman spectra for solutions with various concentrations (a) SO$_4^{2-}$; (b) HCO$_3^-$; (c) CO$_3^{2-}$; and (d) linear fitting for calibration models. (Adapted with permission from Publication 2. Copyright 2023 the authors, published by Elsevier.)

As shown in Equations 3.2 to 3.9, the regression coefficients for the calibration models are close to unity, indicating that the models have good accuracy for concentration determination. For measuring ion concentration in a concentrated solution, UV-VIS and Raman have significant advantages in that sample preparation and measurements are simple and results have good accuracy, which avoids errors deriving from sample dilution.
4. Results and discussion

The main results are presented and discussed in this chapter. First, the saturation vapor pressures for cobalt sulfate solutions at different concentrations and temperatures are presented. The solubility of cobalt sulfate in water with additions of various impurities in a temperature range of 5 °C to 40 °C are shown. Second, the factors affecting the evaporative and cooling crystallization are described. Moreover, the nucleation kinetics of CoSO₄ in batch cooling crystallization and the crystallization kinetics of CoSO₄ in a continuous MSMPR system are also examined. The hydrate forms of CoSO₄ obtained in the experiments and its dehydration during the drying process are elaborated. Finally, the precipitation of CoCO₃ and its precipitation behavior are explored.

4.1 Thermodynamics of CoSO₄ solution

Thermodynamic studies which include the vapor pressure of CoSO₄ solution and CoSO₄ solubility are needed to explore the vacuum evaporative crystallization and cooling crystallization of CoSO₄.

4.1.1 Vapor pressure of CoSO₄ solution

In vacuum evaporative crystallization, the solution was boiled at a certain temperature (boiling point also crystallization temperature) by adjusting the reactor pressure to the vapor pressure of the solution. Using Aspen Plus and experimental measurements, the vapor pressures of solutions containing different concentrations of CoSO₄ were estimated at temperatures of 30 °C, 40 °C, 60 °C, and 80 °C. Electrolyte non-random two-liquid (E-NRTL) model was applied for vapor-liquid equilibrium prediction in Aspen Plus, and the default parameters of E-NRTL from Aspen database were adopted. For comparison, the vapor pressure of pure water was obtained from the literature [88]. Based on the results shown in Figure 4.1, the predicted vapor pressure is in good agreement with the experimental results. The vapor pressure of the saturated CoSO₄ solution was 35 mbar, 64 mbar, 174 mbar, and 423 mbar at temperatures of 30 °C, 40 °C, 60 °C, and 80 °C, respectively. Compared with the results for water, and as expected based on Raoult's law, it was found that the presence of dissolved CoSO₄ decreased the vapor pressure of the solution, and the pressure difference between water and CoSO₄ became larger as the CoSO₄ concentration increased.
Results and discussion

Figure 4.1 Vapor pressure of saturated CoSO$_4$ solution and water at various temperatures. (Adapted with permission from Publication 1. Copyright 2022 the authors, published by Elsevier.)

4.1.2 Solubility of CoSO$_4$ in aqueous solutions

The solubility of cobalt sulfate in water with the addition of various impurities (NiSO$_4$, H$_2$SO$_4$) was measured in the temperature range between 5 °C and 40 °C using an isothermal method, as shown in Figure 4.2. It can be seen that the measured CoSO$_4$ solubility in pure water shows good consistency with the literature data which verified the accuracy of UV-VIS for Co concentration measurement and the applied isothermal method. The solubility of CoSO$_4$ rises with an increase in temperature. However, the solubility continuously decreased as the concentration of H$_2$SO$_4$ increased between 0 and 0.6 m or as the concentration of NiSO$_4$ rose within the range of 0 to 0.4 m. This decrease may be caused by the common ion effect of SO$_4^{2-}$ which dissociated from the H$_2$SO$_4$, NiSO$_4$ and CoSO$_4$. It was also found that NiSO$_4$ had a greater impact on CoSO$_4$ solubility compared to the impact of H$_2$SO$_4$. Not only did the CoSO$_4$ solubility decrease, but the slope of solubility against temperature also changed when NiSO$_4$ was present in the solutions. This indicates that a greater temperature difference is required to obtain a similar crystal yield in the presence of Ni compared to pure or acidic cobalt sulfate solutions in cooling crystallization. The measured solubilities give a solid foundation for further studies on cooling crystallization and its kinetics.
Results and discussion

Figure 4.2 Solubility of CoSO$_4$ with addition of NiSO$_4$ and H$_2$SO$_4$ determined by the isothermal method. (Adapted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)

4.2 Vacuum evaporative crystallization of CoSO$_4$

This section contains the results from the investigation of the influence of operating conditions on vacuum evaporative crystallization of CoSO$_4$. The experiments involved testing different crystallization temperatures, heating inputs, and mixing speeds. As is commonly known, cobalt sulfate can exist in three hydrate forms (CoSO$_4$·7H$_2$O, CoSO$_4$·6H$_2$O, and CoSO$_4$·H$_2$O). The specific hydrate form of the crystallized product depends greatly on the crystallization temperature, but crystallization kinetics may also play a role. The XRD patterns, CSD, and SEM images of solid samples obtained at various temperatures are presented in Figures 4.3(a), (b), and 4.4, respectively. The results indicate that cobalt sulfate crystallized as heptahydrate at temperatures of 30 °C and 40 °C, while a lower hydration degree CoSO$_4$·6H$_2$O was obtained at higher temperatures of 60 °C and 80 °C. The effect of temperature on the CSD of the crystallized products was minimal. The average particle size of the solid samples was similar, although the CSD of samples obtained at 60 °C and 80 °C exhibited a wider distribution compared to the samples obtained at 30 °C and 40 °C. The SEM images revealed that the morphology of the samples crystallized at 30 °C and 40 °C resembled an octahedron crystal shape, while no uniform shape was observed for samples obtained at 60 °C and 80 °C. Additionally, it was seen that agglomerates were formed at all of the crystallization temperatures studied, and the agglomeration tendency became greater at higher temperatures. This can be
Results and discussion

attributed to the higher CoSO$_4$ concentration in the solution at higher temperatures, which promotes agglomeration.

In addition to temperature, the effects of heating input and mixing speed on the CSD were also investigated. The results are displayed in Figures 4.3(c) and (d), respectively. The heating input, controlled by adjusting the temperature difference between the heating jacket and solution, had a significantly effect on the CSD of the solid samples. The solid sample obtained from a temperature difference of 10 °C exhibited the largest crystal size and the most uniform CSD. As the temperature difference increased, the crystal size of the solid samples decreased and the CSD became broader. The larger temperature difference provided more heat input for evaporation, thereby enhancing water evaporation. The increased evaporation flux results in a greater level of supersaturation, which enhances both the nucleation and the growth rate of crystals. When nucleation takes control of crystallization, there is a considerable rise in the proportion of smaller crystals within the final crystalline product.

![Figure 4.3 Factors affecting the evaporative crystallization of CoSO$_4$: (a) XRD analysis of products obtained from various temperatures; CSD of solid samples obtained from various (b) temperatures; (c) heating inputs; (d) mixing speeds. (Adapted with permission from Publication 1. Copyright 2022 the authors, published by Elsevier.)](image)

Mixing speed has a great impact on the CSD of a solid sample. It was observed that the particle size decreased as the mixing speed increased, as illustrated in
Figure 4.3(d). The mixing speed enhances both heat and mass transfer in the reactor, leading to improved evaporation and a higher degree of supersaturation, thereby promoting nucleation. Additionally, the higher mixing speed facilitates secondary nucleation resulting from collisions between the crystals and the stirrer. More results and discussion related to the condition effects on the evaporation flux and product yield are presented in Publication 1.

Figure 4.4 SEM images for solid samples obtained from temperatures of (a) 30 °C; (b) 40 °C; (c) 60 °C; (d) 80 °C. (Reprinted with permission from Publication 1. Copyright 2022 the authors, published by Elsevier.)

4.3 Batch cooling crystallization of CoSO$_4$

As CoSO$_4$ solubility shows a decrease with a drop in temperature, cooling crystallization could be an alternative option for recovering Co from aqueous solutions. In this section, the batch cooling crystallization of CoSO$_4$ without seeding was investigated. Moreover, the primary nucleation kinetics of CoSO$_4$ was also studied by measuring the MSZW and induction time.
4.3.1 Cooling rate and impurity effect on the CSD

The influence of cooling rate and impurity concentration ($H_2SO_4$) on the properties of the crystallized product was evaluated. The CSD of solid products obtained from different cooling rates and $H_2SO_4$ concentrations is illustrated in Figures 4.5(a) and (b), respectively. Figure 4.5(a) demonstrates that the CSD decreases with an increased cooling rate. This is because a higher cooling rate leads to a broader MSZW, resulting in a higher supersaturation level at the nucleation temperature and consequently a higher nucleation rate. Furthermore, Figure 4.5(b) indicates that the CSD becomes smaller as the $H_2SO_4$ concentration increases from 0 to 0.6 m. The average size of the crystals decreases from 498 μm to 296 μm. Images of crystals obtained from solutions without and with 0.2 m $H_2SO_4$ are shown in Figures 4.5(c) and (d), respectively. Most of the particles derived from the pure CoSO$_4$ solution typically exhibit an octahedral morphology. On the other hand, particles obtained from a solution with 0.2 m sulfuric acid have a shape that is closer to cubic. These particles also have a higher tendency to aggregate.

Figure 4.5 CSD for solid samples obtained from different (a) cooling rates; (b) $H_2SO_4$ concentrations; and images of solid samples obtained from solution (c) without $H_2SO_4$; and (d) with 0.2 molality $H_2SO_4$. (Adapted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)

4.3.2 Factors affecting the MSZW

In cooling crystallization, the MSZW plays an important role for operation strategy design in that the optimal cooling crystallization is also controlled to form within the metastable zone. Seeding within the metastable zone could control
the supersaturation degree for nucleation, which further controls the CSD of products. In this section, the MSZW for CoSO₄ cooling crystallization was measured under different temperatures, cooling rates, mixing speeds, and H₂SO₄ concentrations.

Figure 4.6 shows the MSZW of a CoSO₄ aqueous solution under different cooling rates and saturation temperatures. The graph demonstrates that the MSZW widens as the cooling rate increases from 3 K/h to 15 K/h. This expansion occurs due to a delay in the cluster size of CoSO₄ molecules when the solution composition changes. Conversely, the MSZW narrows when the saturation temperature rises from 293.15 K to 313.15 K. The increase in saturation temperature leads to a significant rise in the solubility of cobalt sulfate, resulting in an increased number of molecules per unit area and a higher probability of collision. Furthermore, higher solution temperatures facilitate ion-ion collision and mass transfer, thereby promoting nucleation and reducing the MSZW.

Figure 4.6 MSZW of CoSO₄ under different cooling rates and saturation temperatures (mixing speed of 300 rpm) (Reprinted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)

The effects of mixing speed and H₂SO₄ concentration on the MSZW were investigated at a cooling rate of 12 K/h. The results are presented in Table 4.1. It was observed that the MSZW of CoSO₄ decreased as the mixing speed increased from 300 rpm to 500 rpm. This may be because of the enhanced heat and mass
transportation and collisions in the solution that can be attributed to the synergistic effect of agitation. The higher mixing speed promotes nucleation and reduces the MSZW. Likewise, the addition of H₂SO₄ also had a similar impact on the metastable zone, resulting in a narrower width with increasing concentration. The addition of H₂SO₄ affected the solubility of CoSO₄, as shown in Figure 4.2. With a higher sulfuric acid concentration, the slope of linear fitting of solubility against temperature increased, which means that the supersaturation levels increased with the same temperature difference, therefore resulting in a greater driving force for nucleation. Additionally, H₂SO₄ alters the solution composition, similarly, to changes in ion activity, pH, or ion species. For example, SO₄²⁻ can be converted to HSO₄⁻ with increased H₂SO₄ concentration, which could influence the MSZW.

Table 4.1 MSZW of CoSO₄ under different mixing speeds and H₂SO₄ concentrations (cooling rate of 12 K/h). (Adapted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)

<table>
<thead>
<tr>
<th>H₂SO₄ concentration mol/kg water</th>
<th>Mixing speed rpm</th>
<th>T_sat K</th>
<th>T_nucl K</th>
<th>ΔT_max K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300</td>
<td>298.15</td>
<td>281.07 ± 0.38</td>
<td>17.08 ± 0.38</td>
</tr>
<tr>
<td>0</td>
<td>400</td>
<td>298.15</td>
<td>281.99 ± 0.43</td>
<td>16.16 ± 0.43</td>
</tr>
<tr>
<td>0</td>
<td>500</td>
<td>298.15</td>
<td>282.71 ± 0.51</td>
<td>15.44 ± 0.51</td>
</tr>
<tr>
<td>0.1</td>
<td>300</td>
<td>303.15</td>
<td>288.95 ± 0.59</td>
<td>15.20 ± 0.59</td>
</tr>
<tr>
<td>0.2</td>
<td>300</td>
<td>303.15</td>
<td>288.09 ± 0.73</td>
<td>15.06 ± 0.73</td>
</tr>
<tr>
<td>0.4</td>
<td>300</td>
<td>303.15</td>
<td>288.56 ± 0.51</td>
<td>14.59 ± 0.51</td>
</tr>
<tr>
<td>0.6</td>
<td>300</td>
<td>303.15</td>
<td>288.93 ± 0.43</td>
<td>14.22 ± 0.43</td>
</tr>
</tbody>
</table>

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

4.3.3 Nucleation kinetics of CoSO₄ in pure solution from the MSZW

Based on the experimental data of MSZW shown in Figure 4.6, both the SCNL and C3DN approach were adopted for nucleation kinetics estimation in this thesis [108–111].

The expression of nucleation in the SCNL approach is as in the following Equation 4.1:

\[ J = K (lnS)^m \] (4.1)
where \( K \) is the nucleation constant \((#/\text{m}^3\text{-s})\), \( m \) is the apparent order of nucleation, and \( S \) represents the relative supersaturation, calculated as the concentration of CoSO\(_4\) at saturation temperature \((C_{\text{sat}})\) divided by the concentration of CoSO\(_4\) at nucleation temperature \((C_{\text{nuc}})\). The parameters \( K \) and \( m \) were estimated by building a linear relationship between the cooling rate and maximum supercooling ratio \( \Delta T_{\text{max}}/T_{\text{sat}} \) as Equation 4.2. The values of \( K \) and \( m \) were calculated from intercept \( \varphi \) and slope \( \beta \), respectively.

\[
\ln \left( \frac{\Delta T_{\text{max}}}{T_{\text{sat}}} \right) = \varphi + \beta \ln R \tag{4.2}
\]

In the C3DN approach, the nucleation rate is expressed as Equation 4.3:

\[
J = A \exp \left[ -\frac{B}{(\ln S)^2} \right], \tag{4.3}
\]

where \( A \) is the pre-exponential factor \((#/\text{m}^3\text{-s})\) and \( B \) is the thermodynamic parameter related to nuclei formation. The values of \( A \) and \( B \) were determined by building a linear relationship between the \((T_{\text{sat}}/\Delta T_{\text{max}})^2\) and \( \ln R \), according to Equation 4.4. The solid-liquid interfacial energy \( \gamma \) can be calculated from \( B \) value using Equation 4.5.

\[
\left( \frac{T_{\text{sat}}}{\Delta T_{\text{max}}} \right)^2 = F - F_1 \ln R, \tag{4.4}
\]

\[
\gamma = \left( \frac{3Bk_BT^3}{16\pi\Omega^2} \right)^{1/3}, \tag{4.5}
\]

where \( F \) and \( F_1 \) is the intercept and slope, respectively, in Equation 4.4; \( k_B \) is the Boltzmann constant, \(1.380649\times10^{-23}\ \text{J}\cdot\text{K}^{-1}; \) \( \Omega \) is the molecular volume of CoSO\(_4\cdot7\text{H}_2\text{O}, \; 2.396 \times 10^{-28}\ \text{m}^3/\text{mol.} \)

The kinetic parameters determined by the SCNL approach and C3DN approach are listed in Tables 4.2 and 4.3, respectively. The detailed calculation process is explained in Publication 3.

As presented in Table 4.2, there is an observed decline in the apparent nucleation order \( m \) from 2.266 to 1.249 as the saturation temperature increases. These findings align with the findings of Nývlt et al., who stated that the apparent nucleation order for inorganic compounds falls within the range of 0.98 to 8.3. Additionally, the data illustrates that the values of the nucleation constant \( K \) remain relatively consistent across varying saturation temperatures. It is also possible to estimate the nucleation rate \( J \) for different saturation temperatures and supersaturations. The outcomes suggest that the nucleation rate escalates as the saturation temperature rises at the same level of supersaturation. The findings presented in Table 4.3 indicate that there is a positive correlation between the saturation temperature and the kinetic parameter \( A \). Consequently,
an elevated saturation temperature has the potential to expedite the rate of nucleation by inducing a higher generation of supersaturation and facilitating faster mass and energy transformation. Additionally, a rise in the saturation temperature is observed to be accompanied by a decrease in the interfacial energy \( \gamma \). This outcome provides evidence that a higher saturation temperature can promote a smoother occurrence of the nucleation process. As a result, it is reasonable to expect that the MSZW would become narrower with higher saturation temperatures.

Table 4.2 Kinetic parameters for SCNL approach. (Adapted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)

<table>
<thead>
<tr>
<th>( T_{\text{sat}} (K) )</th>
<th>( m = 1/\beta )</th>
<th>( \varphi )</th>
<th>( K \times 10^{28}, # / m^3 s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>2.028</td>
<td>-0.070</td>
<td>9.677</td>
</tr>
<tr>
<td>298.15</td>
<td>1.946</td>
<td>-0.024</td>
<td>11.187</td>
</tr>
<tr>
<td>303.15</td>
<td>1.667</td>
<td>0.418</td>
<td>8.898</td>
</tr>
<tr>
<td>308.15</td>
<td>1.548</td>
<td>0.523</td>
<td>10.331</td>
</tr>
<tr>
<td>313.15</td>
<td>1.249</td>
<td>1.009</td>
<td>11.287</td>
</tr>
</tbody>
</table>

Table 4.3 Kinetic parameters for C3DN approach. (Adapted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)

<table>
<thead>
<tr>
<th>( T_{\text{sat}} (K) )</th>
<th>( F )</th>
<th>( F_l )</th>
<th>( B )</th>
<th>( A \times 10^{26}, # / m^3 s )</th>
<th>( \gamma ) (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>-2813.10</td>
<td>552.17</td>
<td>0.037</td>
<td>3.974</td>
<td>1.363</td>
</tr>
<tr>
<td>298.15</td>
<td>-3832.00</td>
<td>737.17</td>
<td>0.027</td>
<td>4.258</td>
<td>1.245</td>
</tr>
<tr>
<td>303.15</td>
<td>-6505.70</td>
<td>1205.80</td>
<td>0.016</td>
<td>4.407</td>
<td>1.063</td>
</tr>
<tr>
<td>308.15</td>
<td>-10221.00</td>
<td>1880.60</td>
<td>0.010</td>
<td>4.688</td>
<td>0.921</td>
</tr>
<tr>
<td>313.15</td>
<td>-31164.00</td>
<td>5681.30</td>
<td>0.003</td>
<td>5.095</td>
<td>0.641</td>
</tr>
</tbody>
</table>

4.3.4 Factors affecting induction time

The induction time for CoSO₄ batch cooling crystallization from aqueous solution was measured using the isothermal method described in Section 3.4.2. The effects of nucleation temperature and degree of supersaturation on the induction time were investigated and the results are shown in Figure 4.7(a). It can be clearly seen that the induction time decreases drastically as the supersaturation increases. Furthermore, a notable decrease in the induction time is observed as
the nucleation temperature rises. The impact of H₂SO₄ concentration on the induction time was also examined, and the results are presented in Figure 4.7(b). They demonstrate a continuous decrease in the induction time as the sulfuric acid concentration increases. These findings align with the MSZW measurement provided in Section 4.3.2. The reduction in induction time can be primarily attributed to higher levels of supersaturation and potentially the modification of solution structure resulting from the addition of H₂SO₄.

Figure 4.7 Induction time of CoSO₄ at (a) various supersaturation levels and nucleation temperatures; (b) different H₂SO₄ concentrations with the same undercooling (ΔT = T_{sat} - T_{nucl} = 303.15 - 293.15 = 10 K, curve line as a guide to the eye). (Adapted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)
The induction time is usually assumed to be inversely proportional to the nucleation rate. A relationship between induction time and supersaturation can be expressed as Equation 4.6 \[112–114\]. By plotting \(\ln(t_{\text{ind}})\) against \(1/(\ln S)^2\) at a constant temperature, as shown in Figure 4.8, the interfacial energy \(\gamma\) can be calculated by the slope, as listed in Table 4.4.

\[
\ln(t_{\text{ind}}) = K + \frac{16\pi\gamma^2\alpha^2}{3k_BT^2(\ln S)^2}
\]  

(4.6)

In Figure 4.8, two distinct regions of nucleation mechanism can be identified through examination of the level of supersaturation. At lower supersaturation levels \((S < 1.15; [(\ln S)^{-2}] > 51))\), heterogeneous primary nucleation is found to be the dominant mechanism. In contrast, when supersaturation levels exceed 1.15, it seems that unseeded batch crystallization is predominantly governed by the phenomenon of homogeneous primary nucleation. The interfacial energy value, representing the homogeneous nucleation mechanism, was obtained by analyzing the slope of the linear fitting. The results, presented in Table 4.4, demonstrate a slight decrease in \(\gamma\) with an increase in nucleation temperature. This suggests that nucleation becomes more readily achievable at higher temperatures, thus favoring the formation of crystal nuclei.

In summary, the measured MSZW, induction time, and estimated kinetic parameters of nucleation play a critical role in the design and development of a crystallization process. Seeding within the metastable zone is an efficient way to control the crystal properties by controlling the supersaturation for crystallization.

<table>
<thead>
<tr>
<th>(T_{\text{nucl}}) (K)</th>
<th>(\text{Slope})</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>0.169</td>
<td>2.303</td>
</tr>
<tr>
<td>303.15</td>
<td>0.148</td>
<td>2.240</td>
</tr>
</tbody>
</table>
Results and discussion

Figure 4.8 Plots of $\ln(t_{ind})$ versus $1/\ln(S)^2$ at various nucleation temperatures with pure CoSO$_4$ solutions (mixing speed of 300 rpm). (Reprinted with permission from Publication 3. Copyright 2023 the authors, published by Elsevier.)

4.4 Continuous cooling crystallization of CoSO$_4$

Compared with batch processes, the advantages of continuous cooling crystallization are consistent product quality, high productivity and efficiency, and low investment costs. This section describes the continuous cooling crystallization of CoSO$_4$ that was conducted in an MSMPR crystallizer. The effects of various factors on the product properties and crystallization kinetics are demonstrated. Mathematic models for nucleation and growth rates were developed. The results are shown in detail in Publication 4.

4.4.1 Factors affecting product CSD

An investigation was made of the effects of residence time, suspension density, temperature, and mixing speed on the CSD of products obtained under steady state conditions. The results are displayed in Figures 3 and 5, respectively, in Publication 4. It was observed that the crystal size increases with longer residence time, higher temperature, or suspension density, while it decreases with increasing mixing speed. A longer residence time allows more time for crystal growth, and a higher crystallization temperature facilitates the movement of solute molecules or ions, promoting crystal growth. A higher suspension density leads to the higher agglomeration tendency which increases the particle size. On
the other hand, increased mixing speed leads to more collisions between crystals, stirrers, and the reactor, resulting in an increase in the particle breakage and secondary nucleation rate and a decrease in CSD. The influence of impurities (NiSO$_4$ and H$_2$SO$_4$) on the CSD of the products was also evaluated. In Publication 4, Figure 3(d) shows the CSD, while Figure 4 displays the microscopy images of the products obtained with various concentrations of impurities. In Figure 3(d), it can be observed that the crystal size did not change significantly when 0.2 m of NiSO$_4$ was added as an impurity. However, with a further increase in impurity concentration, the crystal size continuously decreased, with the average crystal size reducing from 329.58 µm to 288.28 µm. The microscopy images of the crystal samples also support the findings of the CSD analysis. When a concentration of 0.3 m of NiSO$_4$ and 0.4 m of NiSO$_4$ were added, along with 0.2 m of H$_2$SO$_4$, the crystal size clearly decreased, and the aggregation phenomena became more pronounced.

### 4.4.2 Factors affecting kinetics

The nucleation and growth rates could be estimated from the experimental CSD data using population balance equations under the assumptions of the MSMPR theory [115]. One of the widely used solutions for PBEs can be expressed as Equations 4.7- 4.9:

\[
\ln n = \ln n^0 - \frac{L}{\tau}, \quad (4.7)
\]

\[
n^0 = \frac{B^0}{G}, \quad (4.8)
\]

\[
n_i = \frac{\nu_i(c_0 - c)}{k_v \rho_c \Delta L_i L_{i,av}} = \frac{\nu_i M_T}{k_v \rho_c \Delta L_i L_{i,av}^{3/2}}, \quad (4.9)
\]

where $n$ is the population density, expressed in #/m$^3$-µm; $\tau$ is the mean residence time, in s; $L$ is the crystal size, in µm; $n^0$ is the nuclei population density, in #/m$^3$-µm; $M_T$ is the suspension density, in kg/m$^3$; $\nu_i$ is the volume fraction of crystals between size channels $L_i$ to $L_{i+1}$; $k_v$ is the crystal shape factor (0.471); $\rho_c$ is the density of crystal CoSO$_4$ (1.948 g/cm$^3$ for the heptahydrate form); $\Delta L_i$ (µm) is the width between the size channels $L_i$ to $L_{i+1}$; and $L_{i,av}$ (µm) is the average crystal size of the i-th channel. Based on the CSD data and the composition of mother liquor at steady state, the population balance in the MSMPR reactor can be calculated using Equation 4.9. Furthermore, the growth rate ($G$) and nucleation rate ($B$) can be estimated by building the linear relationship between $\ln (n)$ and $L$, as in Equations 4.7 and 4.8. The nucleation and growth rates under different suspension densities, supersaturations, and temperatures were calculated, as shown in Figure 4.10. The detailed calculation process is illustrated in Publication 4.
As depicted in Figures 7(a) and (b) of Publication 4, the nucleation rate exhibits a positive correlation with both suspension density and supersaturation. Increasing the suspension density leads to the formation of more particles in the crystallizer, thereby enhancing the collisions between crystals, stirrer, and crystallizer and promoting secondary nucleation. Additionally, a higher supersaturation provides a greater driving force for crystal nucleation. Figure 8(a) of Publication 4 demonstrates that the crystal growth rate increases with increasing supersaturation. Conversely, the crystallization temperature has opposite effects on nucleation and growth rates. A higher temperature promotes growth but hinders nucleation, as shown in Figures 7(c) and 8(d) of Publication 4. This is because higher temperatures allow the solution to reach equilibrium faster, resulting in a smaller supersaturation that hinders nucleation and growth. On the other hand, the solution concentration increases with rising temperature, which supports crystal growth. Overall, it can be concluded that temperature has a greater impact on crystal growth compared to supersaturation under the investigated conditions.

### 4.4.3 Models for kinetic rate estimation

For the estimation of nucleation and growth rates, the mathematical models can be expressed as Equations 4.10 and 4.11, respectively [89,115]:

\[
B^0 = k_b M_T^j \Delta C^b \quad (4.10)
\]

\[
G = k_g \cdot \Delta C^g = k_{g0} \exp \left( - \frac{E_g}{RT_{cry}} \right) \cdot \Delta C^g \quad (4.11)
\]

The parameters, including the nucleation order for suspension density \((j)\) and supersaturation \((b)\), nucleation rate constant \((k_b)\), growth rate constant \((k_{g0})\), growth order \((g)\), and activation energy for growth \((E_g)\) can be estimated from calculated kinetic data using non-linear regression in Origin software. The models for nucleation and growth rates can be obtained as Equations 4.12 and 4.13, respectively. Suspension density was observed to exert a significant influence on the nucleation rate. An \(j\) value of 2.425 indicated that the secondary nucleation formed by crystal-crystal collision plays the role of cobalt sulfate nucleation in the present study. The values of \(b\) and \(g\) are small, indicating that supersaturation has a minor impact on the crystallization kinetics in this case. A relative kinetic order \((b/g)\) of 3.24 demonstrates that a larger crystal size can be obtained under a small supersaturation with a long residence time [115]. The activation energy of crystal growth is determined from parameter regression, as 27.23 kJ/mol. The regression coefficient values for the nucleation and growth rate models are 0.945 and 0.827, respectively. This shows the developed models have good reliability.
Results and discussion

\[
\left( \frac{B^0}{m^3 s} \right) = 6944.1 \times \left( \frac{M_T}{kg m^3} \right)^{2.425} \times \left( \frac{\Delta C}{g \text{water}} \right)^{0.506} \quad (R^2 = 0.945) \tag{4.12}
\]

\[
\left( \frac{G}{um} \right) = 7048.87 \times \exp \left\{ -\frac{27230.76}{R(T_{cry} / K)} \right\} \times \left( \frac{\Delta C}{g \text{water}} \right)^{0.156} \quad (R^2 = 0.827) \tag{4.13}
\]

The kinetics models show good accuracy when estimating crystal size at steady state. The evaluation and simulation results of the kinetics models are shown in Publication 4. The kinetics data measured from the experiments and models constructed in this study have great utilization value for modeling, design, and operation in the industrial crystallization of CoSO₄.

4.5 Hydrate forms of CoSO₄ and their dehydration in drying

In the investigation of CoSO₄ crystallization, it was found that CoSO₄ is mainly crystallized as heptahydrate at a crystallization temperature equal or lower than 40 °C. The TG-DTA results shown in Figure 4.9(a) further verify this finding. However, crystallized CoSO₄·7H₂O is not stable and could be dehydrated during drying. The weight losses through the drying process at different drying temperatures are presented in Figure 4.9(b), which illustrates that the CoSO₄·7H₂O product lost about 10% weight after drying over 7 days when one molecule of crystalline water was dehydrated. Under drying temperature conditions of 40 °C and 60 °C, there was a weight loss of approximately 38%. This weight loss closely matches the theoretical weight loss of 38.4% for the dehydration of CoSO₄·7H₂O to CoSO₄·H₂O. Moreover, the dehydration took place much faster with a drying temperature of 60 °C.

![Figure 4.9](image)

Figure 4.9 (a) TG-DTA analysis for sample crystallized at 40 °C; (b) weight losses for CoSO₄·7H₂O sample drying at various temperatures. (Adapted with permission from Publication 1. Copyright 2022 the authors, published by Elsevier.)

The XRD patterns for samples obtained at different drying times at drying temperatures of 23 °C, 40 °C, and 60 °C are shown in Figures 4.10(a), (b), and (c),
respectively. The XRD patterns confirmed the findings from weight losses, and the drying process can be summarized as follows: drying temperature of 23 °C: CoSO$_4$$\cdot$7H$_2$O (Original)- CoSO$_4$$\cdot$6H$_2$O (after 48 h); 40 °C: CoSO$_4$$\cdot$7H$_2$O (Original)- CoSO$_4$$\cdot$6H$_2$O (8 h)- CoSO$_4$$\cdot$H$_2$O (24-168 h); 60 °C: CoSO$_4$$\cdot$7H$_2$O (Original)- CoSO$_4$$\cdot$6H$_2$O (8-24 h)- Mixture of CoSO$_4$$\cdot$6H$_2$O and CoSO$_4$$\cdot$H$_2$O (48 h)- CoSO$_4$$\cdot$H$_2$O (168 h).

In this study, Raman spectroscopy was successfully utilized for identifying the hydrate forms of CoSO$_4$. Analyzing the strength of the S-O bond and the chemistry surrounding the SO$_4^{2-}$ ion can be facilitated by the vibrational wavenumber of the $\nu_1$ (SO$_4^{2-}$) mode, as demonstrated by previous research [116–118]. The crystallographic arrangement of cobalt sulfate hydrates reveals that the SO$_4^{2-}$ ion in CoSO$_4$$\cdot$6H$_2$O and CoSO$_4$$\cdot$7H$_2$O exhibits similar chemical environments. In CoSO$_4$$\cdot$XH$_2$O crystal, SO$_4^{2-}$ ions are not only coordinated with Co$^{2+}$ as ligands, but also form complex H-bonding within a lattice and coordinated H$_2$O. With the number of crystal water (value of X) in CoSO$_4$$\cdot$XH$_2$O crystal decreases, the H-bond between SO$_4^{2-}$ and H$_2$O is less extensive. The coordination of SO$_4^{2-}$ and the strength of H-bonding influence the peak position of the $\nu_1$ (SO$_4^{2-}$) mode. By comparing the XRD patterns (Figure 4.10(b)) and the Raman spectra for the $\nu_1$ (SO$_4$) mode (Figure 4.11) for samples dried at 40 °C, the observed changes in the $\nu_1$ (SO$_4$) mode can be attributed to the dehydration process. Specifically, wave numbers of 984.3 cm$^{-1}$, 990.3 cm$^{-1}$, and 1022.4 cm$^{-1}$ were associated with heptahydrate, hexahydrate, and monohydrate for cobalt sulfate, respectively.

For identifying the cobalt sulfate hydrate forms, the color of the sample also indicates the hydrate form quite clearly. As shown in Figure 4.12, the sample color changes from red to pink and then reddish as cobalt sulfate hydrates transform from heptahydrate to hexahydrate and then to monohydrate.
Figure 4.10 XRD patterns for samples drying at different temperatures: (a) 23 °C; (b) 40 °C; (c) 60 °C. (Adapted with permission from Publication 1. Copyright 2022 the authors, published by Elsevier.)
Results and discussion

4.6 CoCO₃ precipitation

CoCO₃ precipitation was conducted by adding CoSO₄ solution to the Na₂CO₃ solution. The effects of the operating conditions on precipitation were investigated. In addition, the precipitation mechanism was explored by offline Raman spectroscopy and PXRD, and inline FBRM and pH measurement. The impact of pH on precipitation was investigated by adjusting the concentration of H₂SO₄ in the initial CoSO₄ solution. The final pH of precipitation was
6.5-7.2 as the H$_2$SO$_4$ concentration was varied from 0.5 m to 0.2 m. To determine the effect of pH on the precipitate phases, PXRD analysis was conducted, and is shown in Figure 4.13(a). The precipitate obtained at pH 7.2 consisted of CoCO$_3$ and Co$_2$CO$_3$(OH)$_2$, albeit with low crystallinity. This was determined through the analysis of the diffraction peaks, which revealed that the peaks at approximately 15°, 18°, and 35° aligned with the characteristic peaks of Co$_2$CO$_3$(OH)$_2$. However, when the solution pH was below 7, these peaks disappeared and were replaced by CoCO$_3$ peaks. This finding suggests that the primary phase of the precipitate transformed into cobalt carbonate within the pH range of 6.5 to 7. The pH also has a great impact on the cobalt precipitation efficiency, as shown in Table 4.5. The Co precipitation efficiency decreased from about 100% to around 91%, with the final pH decreasing from 7.2 to 6.5. This is because the precipitates (Co$_2$CO$_3$(OH)$_2$, and CoCO$_3$) could be dissolved in an acidic solution.

The temperature of precipitation also affects the phases of the precipitates and the efficiency of precipitation. Figure 4.13(b) shows that the precipitates consist mainly of cobalt carbonate during precipitation, and their crystallinity improves as the temperature is increased from 40 °C to 65 °C. Furthermore, the peaks marked with arrows in Figure 4.13(b) correspond to cobalt carbonate hydrate formation at higher precipitation temperatures. The higher temperature facilitates the conversion of HCO$_3^-$ into CO$_2$ and OH$,^-$, and the increased concentration of OH$,^-$ enhances the precipitation of cobalt carbonate hydroxide. Table 4.6 shows that a higher temperature is advantageous for the precipitation of cobalt carbonate.

| Table 4.5. Cobalt precipitation efficiency at various final pH values. |
|---------------------------------|--------|--------|--------|--------|
| Final pH                       | 7.2    | 7.0    | 6.7    | 6.5    |
| Co precipitation efficiency %  | 101.42 | 99.96  | 91.01  | 91.38  |

| Table 4.6. Cobalt precipitation efficiency at various temperatures. |
|---------------------------------|--------|--------|--------|--------|
| Temperature °C                  | 40     | 50     | 60     | 65     |
| Co precipitation efficiency %  | 90.82  | 91.01  | 96.03  | 96.06  |
To investigate the mechanism of precipitation, several samples were collected and analyzed at different pH levels. The FBRM results and pH changes during precipitation are presented in Figure 4.14. The pH and time of sample collection were labeled as numbers 1-7. The asterisk and diamond symbols indicate the start and end points of reactant addition, respectively. The pH curve exhibits a
three-stage decrease with the addition of CoSO$_4$ solution. Initially, there is a significant drop in pH, which can be attributed to the neutralization of free H$^+$ and OH$^-$. Subsequently, the pH decrease becomes slower, suggesting that the main reaction during this period could be the conversion of carbonate to bicarbonate or even carbonic acid. In the final stage, the pH decreases rapidly, indicating that OH$^-$ and CO$_3^{2-}$ are consumed by precipitation and the H$^+$ in the solution cannot be neutralized. The count rates determined by FBRM also show different stages of precipitation. Upon the addition of CoSO$_4$ solution, precipitation begins immediately, although the rate of precipitation is low, and the count rates increase slowly. After the pH decreases to below 8.5, the count rates exhibit a significant increase, indicating that precipitation is occurring rapidly. This change in count rate may also indicate the phase change of the precipitates.

![Figure 4.14](image-url)  
Figure 4.14. Count rates obtained by FBRM and pH trends during precipitation. (Reprinted with permission from Publication 2. Copyright 2023 the authors, published by Elsevier.)

Samples 1-7 were collected and then filtered. The mother liquor of samples 1-7 was analyzed by Raman spectroscopy for concentration measurement of anions. Solid samples 1-7 were analyzed by PXRD and SEM. The results are shown in Figures 4.15, 4.16, and 4.17, respectively.

Figure 4.15 indicates that concentration of CO$_3^{2-}$ decreased as the pH value decreased. It reached zero when the pH values were lower than 7. On the other hand, the concentration of HCO$_3^-$ showed a different trend. It initially increased and then decreased. The highest concentration of bicarbonate was observed in
sample 4, which had a pH value of 8.5. Furthermore, the concentration of total carbon ions supported the findings from the FBRM results, indicating that precipitation occurred rapidly after the pH dropped below 8.

Figure 4.15. Raman analysis of mother liquor samples 1-7 obtained during precipitation: (a) Raman spectrum; (b) concentration of anions calculated from Raman calibration models. (Reprinted with permission from Publication 2. Copyright 2023 the authors, published by Elsevier.)

Figure 4.16 displays the XRD patterns for samples 2-7 and the final precipitate. XRD analysis for sample 1 could not be conducted due to the small amount of the sample. The results indicate that cobalt was initially precipitated as \( \text{Co}_2\text{CO}_3(\text{OH})_2 \), and as the pH decreased, more cobalt precipitated as \( \text{CoCO}_3 \). At
a pH of 7, CoCO$_3$ became the main solid phase in the precipitate. This finding aligns well with the ion concentration shown in Figure 4.15(b), which indicates that the consumption of carbonate is low at pH levels higher than 8.

Figure 4.16. PXRD patterns for solid samples 2-7 and final product collected from precipitation. (Reprinted with permission from Publication 2. Copyright 2023 the authors, published by Elsevier.)

The SEM images of samples 1-7 and the final precipitate reveal a clear change in morphology. Figure 4.17 illustrates the initial stage of the precipitate, where it primarily consists of large aggregates of individual needle-shaped particles. As the pH decreases, more spherical particles are observed in the precipitates, indicating more cobalt precipitated as CoCO$_3$. Finally, the majority of the precipitated particles assume a spherical form and exist as single crystals or their aggregates. PXRD analysis identified these particles as cobalt carbonate.
Results and discussion

Figure 4.17 SEM images for solid samples: (a)-(g) refer to samples 1-7; (h) the final precipitate. (Reprinted with permission from Publication 2. Copyright 2023 the authors, published by Elsevier.)
The pH level has a notable effect on cobalt carbonate precipitation, as indicated by the results obtained from various analyses. The precipitation process is influenced by pH levels decreasing from 11 to around 7. Initially, cobalt precipitates as $\text{Co}_2\text{CO}_3(\text{OH})_2$. Subsequently, a mixture of $\text{Co}_2\text{CO}_3(\text{OH})_2$ and $\text{CoCO}_3$ forms, and finally $\text{CoCO}_3$ is obtained. The presence of carbon species in the solution also varies with the pH changes. It was observed that $\text{CoCO}_3$ precipitation occurred when bicarbonate was predominantly present in the solution.
5. Summary

In the present work, the crystallization of cobalt salts for recovering Co from aqueous solutions was investigated comprehensively. The evaporative and cooling crystallization of CoSO₄ and cobalt carbonate precipitation were successfully carried out. In addition, cobalt sulfate solubility in aqueous solution with various impurities was measured. The kinetics of CoSO₄ cooling crystallization were also determined for both batch and continuous processes. Based on the results presented, the following conclusions can be made:

- Vacuum evaporative crystallization is a feasible method for recovering cobalt sulfate from aqueous solutions. The vapor pressure of CoSO₄ solution varies with temperature and concentration. Temperature affects the hydrate forms of crystallized CoSO₄, where CoSO₄·7H₂O crystallizes in a temperature range between 30 °C and 40 °C, while CoSO₄·6H₂O crystallizes at 60 °C to 80 °C. Evaporation is enhanced by higher heat energy input and mixing speed, which affect the solution supersaturation and result in smaller crystal sizes.

- The solubility of CoSO₄ increases with an increase in temperature but decreases with a rise in impurity concentration (NiSO₄, H₂SO₄). In the unseeded batch cooling of CoSO₄, a higher concentration of sulfuric acid and a faster cooling rate can increase the MSZW and the supersaturation at the nucleation temperature, resulting in a smaller crystal size. The MSZW of CoSO₄ batch cooling crystallization increases when the saturation temperature, mixing speed, and H₂SO₄ concentration decrease, or when the cooling rate increases. The determination of the induction time for pure cobalt sulfate solution indicates that homogeneous primary nucleation dominates at high supersaturation levels (S > 1.15), while heterogeneous primary nucleation dominates at low supersaturation levels (S < 1.15). Kinetic models based on the MSZW and induction time approaches show good consistency in describing the nucleation of CoSO₄.
Continuous cooling crystallization of CoSO$_4$ from aqueous solutions was successfully carried out in an MSMPR crystallizer. The mean crystal size at steady state increased with an increase in residence time and crystallization temperature; however, it decreased with a rise in impurity concentration and mixing speed. The kinetic models developed using PBEs indicated that the nucleation rate strongly depends on the suspension density. The order of suspension density for nucleation suggests that secondary nucleation caused by crystal-crystal collisions plays a significant role in CoSO$_4$ nucleation. The established models for nucleation and growth rates provide reliable predictions for crystal size distribution.

CoSO$_4$ is primarily crystallized in the heptahydrate form at temperatures below 40 °C and can be easily dehydrated. At 23 °C, CoSO$_4$$\cdot$7H$_2$O undergoes dehydration and stabilizes as CoSO$_4$$\cdot$6H$_2$O. The dehydration of CoSO$_4$$\cdot$7H$_2$O is almost complete at 40 °C and 60 °C leading to formation firstly of CoSO$_4$$\cdot$6H$_2$O and finally of the monohydrate form, CoSO$_4$$\cdot$H$_2$O.

CoCO$_3$ was successfully precipitated by feeding a pure or acidic aqueous solution of CoSO$_4$ into an aqueous solution of Na$_2$CO$_3$. The pH of the solution was found to have a significant influence on the precipitation of CoCO$_3$. As the pH decreased due to the addition of CoSO$_4$ solution, cobalt initially precipitated as Co$_2$CO$_3$(OH)$_2$, followed by a mixture of Co$_2$CO$_3$(OH)$_2$ and CoCO$_3$, and ultimately CoCO$_3$.

Raman spectrometry and UV-VIS spectrophotometry have been found to have significant potential in studying the crystallization of metal salts. Raman spectrometry can be utilized for identifying phases in solid samples as well as quantifying anion concentrations in liquid samples. On the other hand, UV-VIS spectrophotometry offers a straightforward approach for measuring the concentrations of Co and Ni. Raman and UV may have great potential for use as a monitoring and control tool for solutions containing multiple electrolytes. Compared with the commonly used chemical analysis methods, such as Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AAS), the advantage of UV-VIS and Raman in crystallization research is their higher accuracy for measuring ion concentrations in highly concentrated mother liquors since no high fold dilutions are needed in sample preparation.

The results showed that evaporative crystallization, cooling crystallization, or reactive crystallization can be applied for cobalt recovery from aqueous solutions. The produced CoSO$_4$ by evaporative and cooling crystallization and CoCO$_3$ from reactive crystallization are widely utilized in battery industry. A brief comparison between these three technologies is listed at Table 5.1.
Table 5.1 Brief comparison between crystallization methods applied in this thesis.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum Evaporative crystallization</td>
<td>Process is simple; Available for large-scale production; Evaporation in low temperature range;</td>
<td>High cobalt concentration is needed. High energy consumption due to high latent heat of evaporation (2260 kJ/kg). Process control difficult (pressure, evaporation rate)</td>
</tr>
<tr>
<td>Cooling crystallization</td>
<td>Process control simple; Easy to obtain required product properties;</td>
<td>High cobalt concentration is needed (high energy consumption in pretreatment to concentrate initial solution); Limited yield (relatively high cobalt concentration in remained mother liquor);</td>
</tr>
<tr>
<td>Cobalt carbonate precipitation</td>
<td>Lower energy consumption; Suitable for a low cobalt concentration solution</td>
<td>Extra reagents are needed; More impurities involved (Na₂CO₃); Undesired solid phase may form (Co₂CO₃(OH)₂)</td>
</tr>
</tbody>
</table>

The following aspects could be avenues for future studies:

- Further consideration needs to be given to the influence of additional impurities on the crystallization process. The composition of solutions generated from industrial processes is often more complex, with impurities such as Cu, Al, Li, and Na commonly present.
- It is necessary to conduct thermodynamics studies on cobalt in such complex systems. Currently, there is limited thermodynamic data available regarding cobalt in solutions containing various impurities.
- In addition, simulations for scaling-up of cobalt salt crystallization can be conducted using data obtained from these experiments.
References


Cobalt, which has been recognized as a critical raw material, plays a vital role in the energy transition that helps to achieve greenhouse gas neutrality. The demand for cobalt continuously increases and the supply of primary cobalt is surrounding risks. Recovering cobalt from aqueous solutions, such as waste waters, industrial process waters, and side-streams is timely a crucial topic. Crystallization methods, including evaporative, cooling, and reactive crystallization, show great potential for the recovery of cobalt from the aqueous solutions. Moreover, Raman and UV-Vis technologies are efficient, robust, and easy to use for determining the ion's concentrations which is valuable for process monitoring.