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Process monitoring of cobalt carbonate precipitation by reactions between cobalt sulfate and sodium carbonate solutions to control product morphology and purity

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ABSTRACT

Recovering critical elements from EV batteries is challenging as the separation is a complex process which involves different processing parameters. Cobalt (Co) is one of the metals which ensures the life of EV batteries and here we have successfully precipitated cobalt carbonate (CoCO₃) by semi-batch precipitation using cobalt sulfate and sodium carbonate as reactant solutions. The precipitation of cobalt carbonate was investigated by offline Raman spectroscopy, Powder X-ray diffraction analysis, inline Focused Beam Reflectance Measurement (FBRM), and pH measurements. In addition, the effects of various factors including pH, aging time, reactant addition time, mixing speed, and temperature on cobalt carbonate precipitation and the properties of the precipitated solids were investigated. In the process of precipitation, the carbonate ions in the initial electrolyte solution were converted to bicarbonate ions during the addition of acidic cobalt sulfate solution, which consequently decreased the pH in the suspension. When the pH was lower than 8, the carbon mainly existed as bicarbonate and the cobalt carbonate started to precipitate at a high efficiency. Cobalt initially precipitated as cobalt carbonate hydroxide (Co₂CO₃(OH)₂) at a higher pH (9–11) and converted to cobalt carbonate at a lower pH (6.5–8). The crystallite size of cobalt carbonate calculated for the different reaction conditions shows that the growth response is high at longer reactant addition time and high temperature. The morphology of the final cobalt carbonate precipitate was small single spherical crystals and their aggregates. The purity of precipitates could be increased by reducing the aggregation tendency during the precipitation.

1. Introduction

Cobalt carbonate is an important material which is widely utilized as colorants in the ceramic industry (Dohnalová et al., 2014), organic industrial catalysts (Singh, 2018), anode materials in lithium-ion batteries (Huang et al., 2014; Reddy et al., 2014; Su et al., 2013), and precursors for chemical reactions, e.g., for the production of battery-grade cobalt oxides (Du et al., 2013; Nassar, 2013). Cobalt carbonate can be produced by a hydrothermal process (Barceloux and Barceloux, 1999; Cong and Yu, 2009), solvothermal process (Jing et al., 2012), electrodeposition (Lin et al., 2021), or carbonate or bicarbonate precipitation process (Mostafa et al., 2000; Shao et al., 2017; Xue et al., 2011; Zheng et al., 2018). Furthermore, industrial precipitation processes are widely

utilized to recover cobalt from solution as CoCO₃, which is used as a precursor for manufacturing cobalt oxide in the lithium-ion battery industry. This is because raw materials required for precipitation are low cost and easy to obtain, the technology is simple, and the production efficiency is high (Han et al., 2020; Li et al., 2017; Shi et al., 2018). Precipitation from cobalt chloride (Guo et al., 2019a) or nitrate (Nassar and Ahmed, 2011) (raw materials) and ammonium bicarbonate (precipitator) (Guo et al., 2019b; Rahimi-Nasrabadi et al., 2017) solutions have been studied by many researchers, whereas only a few studies have focused on cobalt sulfate solution as a cobalt source. Cobalt sulfate solutions are potential sources for cobalt carbonate precipitation, since sulfuric acid is commonly used for leaching cobalt-bearing materials (Mansur et al., 2022; Wiecka et al., 2020; Xiao et al., 2021). Moreover,

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Abbreviations: FBRM, Focused Beam Reflectance Measurement; PXRD, Powder X-ray Diffraction; SEM, Scanning Electron Microscope; PSD, Particle Size Distribution; AAS, Atomic Absorption Spectroscopy.

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sulfuric acid is widely used as a stripping agent for recovering cobalt from a loaded organic phase in liquid-liquid extraction which is applied frequently in cobalt separation process (Torkaman et al., 2017; Wang et al., 2012). These acidic solutions typically have low pH, varying between 0 and 2 (Kang et al., 2010). It should be pointed out here that the presence of sulfuric acid and other ions as impurities tends to influence cobalt carbonate precipitation. Peng et al. (2020) investigated a twostep process for precipitating spherical cobalt carbonate crystals from dilute cobalt sulfate solution. In their studies, cobalt was first precipitated as cobalt carbonate hydroxide using ammonium carbonate as the precipitant and then converted to cobalt carbonate using hydrothermal treatment in the temperature range of 125 to 150 °C. Furthermore, the sulfur content in the crystalline product was low after hydrothermal treatment. Although the precipitation of cobalt carbonate has been widely investigated in the battery sector, there are very few literature reports that discuss the use of cobalt sulfate and sodium carbonate as raw materials and their impact on the precipitation of cobalt carbonate. Furthermore, the precipitation of CoCO₃ is a multi-step process and different cationic and anionic impurities dominate, based on the processing parameters. Therefore, the preparation of high quality and impurity-free cobalt carbonate by tuning the processing conditions are challenging, yet important.

The changes in pH from alkaline to neutral, causes a change in carbonate species (HCO $_3^-$, CO $_3^{2-}$) which in turn controls the nature of the precipitated solid cobalt carbonate. Depending on the pH and temperature, carbonate ions can convert partially to bicarbonate ions and hydroxide ions with simultaneous hydrolysis in water ($CO_3^{2-} + H_2O \rightleftharpoons$ $HCO_3^- + OH^-$). In alkaline solutions at higher pH, hydroxide ions with carbonate ions will promote the precipitation of cobalt as a double salt of cobalt carbonate hydroxide (Co₂CO₃(OH)₂). With a decrease of pH and hydroxide ion concentration, cobalt starts to precipitate mainly as cobalt carbonate. This leads to the changes in solution composition and the precipitated form of cobalt. The key factors affecting the properties of precipitate are expected to be pH, temperature, reactant addition time, and aging time. Thus, determining concentration of anions in the mother liquor and properties of precipitate is important to ensure the required properties of the final product. Raman spectroscopy is a powerful tool, capable not only of identifying ions, but also quantification (Han and Louhi-Kultanen, 2018; Wu and Zheng, 2010).

The present work focused on the precipitation of cobalt carbonate with aqueous $CoSO_4$ and Na_2CO_3 solutions under different experimental conditions, such as pH, aging time, reactant addition time (feed rate), mixing speed, and temperature. The formation of particles was investigated using online and offline studies. In addition, Raman spectroscopy was applied for the quantitative analysis of anions. The precipitated cobalt crystals were characterized using Powder X-ray diffraction (PXRD), Scanning Electron Microscope (SEM), and Focused Beam Reflectance Measurement (FBRM) to understand the fundamental mechanism of cobalt carbonate precipitation, thus enabling process optimization.

2. Experimental

2.1. Materials and methods

Aqueous solutions used for cobalt precipitation experiments were prepared by dissolving CoSO₄·7H₂O (purity \geq 99%, Acros Organics, AR grade) and Na₂CO₃ anhydrate (purity \geq 99%, Acros Organics, AR grade), respectively. Deionized water was used to prepare all the solutions. The initial pH of the cobalt sulfate solutions was adjusted using technical grade sulfuric acid (purity \geq 95%, VWR Chemicals).

The precipitation experiments were carried out in a 400 mL glass reactor equipped with baffles in an EasyMax 402 stirred tank system (Mettler Toledo). The stirring speed and temperature were adjusted with iControl software. In the experiment, 220 g sodium carbonate solution (1 mol Na₂CO₃ /kg water) was placed in the reactor and 100 g cobalt(II)

sulfate solution (2 mol $CoSO_4$ /kg water) was fed into the reactor with a peristaltic pump at different reactant addition times of 160 min, 400 min, and 800 min (i.e., feed rate of 0.5, 0.2, and 0.1 mL/min). The solution in the reactor was mixed with a tip speed of 0.6, 0.8, and 1.4 m/s (300, 400, and 700 rpm) by using a pitched-blade turbine with four blades (diameter of 38 mm). The precipitation pH was controlled by adjusting the sulfuric acid concentration (0, 0.1, 0.2, and 0.5 mol/kg) in the initial cobalt sulfate solution. The pH value was monitored over time during the whole precipitation process. During the feeding process, slurry samples were taken over time at different pH values to investigate more comprehensively how the precipitation evolved. Precipitates were separated from the mother liquor by vacuum filtration and washed twice with hot deionized rinsing water for further analysis. The mother liquor filtrate was analyzed with a Renishaw inViaTM confocal Raman spectrometer. The crystalline product samples obtained were dried at 60 °C. In addition, FBRM (Particle Track G400) was applied to investigate overall precipitation evolution by monitoring the count rates of various chord length fractions. A schematic diagram of the experimental setup is shown in Fig. 1.

The X-ray powder diffraction data were collected using a Panalytical X'Pert Pro diffractometer with Cu K α_1 radiation ($\lambda = 1.5406$ Å) operated at 40kV. A monochromator was applied to avoid undesired radiation from sample fluorescence. The morphology of the samples was examined using a TESCAN MIRA3 scanning electron microscope. The particle size distribution (PSD) was analyzed with a Malvern Master Sizer 2000 laser diffraction particle size analyzer. The mother liquor obtained during precipitation was analyzed using the Renishaw inViaTM confocal Raman spectrometer to determine the concentrations of anions. A green laser with a wavelength of $\lambda = 532$ nm was used for this measurement. For the liquid samples, the laser beam was set in position using a Leica imaging microscope equipped with an x63 immersion objective lens. The spectra were recorded in the range of 300 to 2000 cm^{-1} with an exposure time of 10 s, 25 mW laser power, and accumulation of five times. The chemical analysis of the precipitated samples was carried out using AAS (Atomic Absorption Spectroscopy, Varian AA240) for cobalt recovery and purification efficiency studies. The precipitated samples were prepared by microwave digestion with a mixture of nitric acid and hydrochloric acid. The cobalt recovery efficiency expressed by the cobalt mass in the precipitates in relation to the cobalt mass in the initial sulfate solution was calculated using Eq. 1:

$$Y = \frac{m_{Co}}{m_{Co}^0} \times 100\% \tag{1}$$

where m_{Co} is the cobalt mass in the precipitate; m_{Co}^0 is the cobalt mass in the initial cobalt sulfate solution.

2.2. Raman quantitative analysis

Since the Raman intensity is directly proportional to the concentration of the corresponding molecules, it can be used for quantitative analysis. To determine the solute concentration, a calibration model was developed between the Raman intensity and the solute concentration (Lin et al., 2020). The Raman intensity depends not only on the concentration, but also on other factors, such as the measurement conditions and the stability of the laser power. Therefore, most quantification methods use an internal standard to correct their influence on the Raman intensity before the construction of a calibration model (Sun and Qin, 2011). In this work, the water band at 1643 cm^{-1} was used as the internal standard (Zhang et al., 2016). The Raman shifts for CO₃²⁻, HCO_3^- , and SO_4^{2-} were traced at 1066, 1015, and 980 cm⁻¹, respectively (Ben Mabrouk et al., 2013; Rudolph et al., 2008). In the studied pH range, HSO₄⁻ ions did not exist, which could also be seen from the Raman results obtained. The standard solutions for building calibration models of CO_3^{2-} , HCO_3^{-} , and SO_4^{2-} were prepared by dissolving Na₂CO₃, Na₂SO₄, and NaHCO3 with known concentrations, respectively. The Raman



Fig. 1. Schematic diagram of the experimental setup for the precipitation of CoCO₃.

spectra for these solutions are shown in Fig.S1(a), (b), and (c), respectively. It can be observed that the Raman characteristic peaks for each anion increased with an increasing concentration. In this case, the peak areas at 1066, 980, and 1015 cm⁻¹ related to the peak area of the water bond (1643 cm⁻¹) were chosen for developing quantitative models of CO_3^{2-} , SO_4^{2-} , and HCO_3^{-} , respectively. The dissociation between HCO_3^{-} and CO_3^{2-} ions were monitored, and the actual concentration was obtained by subtracting the CO_3^{2-} concentration calculated with the CO_3^{2-}

calibration model. The calibration curves and models for CO_3^{2-} , SO_4^{2-} , and HCO_3^- are shown in Fig.S1(d). The regression coefficient of \mathbb{R}^2 is close to 1 indicating that the calibration models are accurate. The analysis of samples obtained from the precipitation process were always carried out with calibration models that had the same conditions during measurement.



Fig. 2. Influence of initial acidity of cobalt sulfate solution on pH evolution. (Temperature of 50 °C, mixing speed of 400 rpm, reactant addition time of 160 min (0.5 mL/min), aging time of 30 min).

3. Results and discussion

3.1. Effect of pH on precipitation

The effect of pH on precipitation was investigated with an aging time of 30 min, temperature of 50 °C, and reactant addition time of 160 min (feed rate of 0.5 mL/min). When cobalt sulfate solution was fed into the sodium carbonate solution, the precipitation was carried out in an alkaline solution. In the crystallizer, the initial pH value of the sodium carbonate solution of about 11.3 changed to the final pH value range of 6.5 to 7.2 when acidic cobalt sulfate solution was added. Fig. 2 shows the trend for pH as a function of time for the precipitation process. The pH continuously decreased until all the acidic CoSO4 solution had been added to the Na₂CO₃ solution, and then the pH started to increase during the aging period. The final pH after feeding decreased from 7.2 to 6.5 with the rise in H₂SO₄ concentration in the initial CoSO₄ solution. The PXRD patterns for precipitates obtained from different end pH values are shown in Fig. 3(a). The precipitate obtained at pH 7.2, as shown in Fig. 3 (a), was cobalt carbonate and cobalt carbonate hydroxide with a low crystallinity. The diffraction peaks located around 15°, 18°, and 35° are in good agreement with the characteristic peaks of cobalt carbonate hydroxide (JCPDS card 29–1416) (Li et al., 2006). When approaching a neutral solution at a pH lower than 7, the peaks for cobalt carbonate hydroxide disappeared and the peaks for cobalt carbonate appeared, which indicated that the main phase for precipitates converted to cobalt carbonate in the pH range between 6.5 and 7. The morphology of the

precipitates obtained at different pH values can be seen in Fig. 4(a)-(d). The crystals of cobalt carbonate were aggregates formed by smaller, spherical shaped, single crystals.

3.2. Effect of aging time on precipitation

Three different aging times were used in this work. Other conditions were maintained at H₂SO₄ concentration of 0.2 mol/kg, reactant addition time of 160 min (feed rate of 0.5 mL/min), and temperature of 50 °C. The PXRD patterns for products precipitated with aging times of 30 min, 180 min, and 360 min are shown in Fig. 3(b). It is clear that the main solid phase of all precipitates is cobalt carbonate anhydrate, and the intensity of the characteristic peaks increased with the increase of aging time, which indicates that an extension of aging time could increase the crystallinity of the precipitate. The SEM images of the precipitates are shown in Fig. 4(c), (e), and (f). The morphologies of the small spherical particles obtained with three aging times were quite similar. However, when the aging time was increased, the degree of aggregation decreased. Thus, the aggregates became smaller and more small single particles could be seen in the particle size analysis. The probable reason for this is the breakage of the aggregate crystals due to collision effects between particles caused by agitation during aging.

3.3. Effect of reactant addition time on precipitation

In the present work, three reactant addition times of 160 min, 400



Fig. 3. PXRD patterns for samples precipitated with different variables: (a) pH; (b) aging time; (c) reactant addition time; (d) temperature (common conditions: mixing speed of 400 rpm in all; 0.2 M H_2SO_4 except in (a); aging time of 30 min except in (b); reactant addition time of 400 min (0.2 mL/min), except in (c); temperature of 50 °C except in (d).

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Fig. 4. Effect of different precipitation conditions on SEM images of the precipitated solids: H_2SO_4 concentration of (a) 0 M, (b) 0.1 M, (c) 0.2 M, (d) 0.5 M; aging time of (e) 180 min, (f) 360 min; reactant addition time of (g) 400 min, (h) 800 min; temperature of (i) 40 °C, (j) and (j') 60 °C, (k) 65 °C; reactant addition time of 160 min (0.5 mL/min) for a, b, c, d and 400 min for others; general conditions, if not varied as above, were H_2SO_4 concentration of 0.2 M, temperature of 50 °C, mixing speed of 400 rpm, and aging time of 30 min.

min, and 800 min which refer to feed rate of 0.5, 0.2, and 0.1 mL/min respectively were used for feeding aqueous acidic CoSO₄ solution with an H₂SO₄ concentration of 0.2 mol/kg. The aging time was 30 min and temperature 50 °C. The PXRD patterns shown in Fig. 3(c) indicated that the precipitated solid was mainly cobalt carbonate. The precipitate obtained with 400 min reactant addition time (feeding rate of 0.2 mL/min) showed high crystallinity. In addition, the characteristic peaks of cobalt carbonate hydroxide double salt located around 15°, 18°, and 35° occurred with a batch time of 800 min (feeding rate of 0.1 mL/min). The morphology of precipitated solids for reactant addition times of 160 min, 400 min, and 800 min can be seen in Fig. 4(c), (g), and (h), respectively. Most of the precipitates were aggregates formed by spherically shaped single particles, which, based on the PXRD results, were mainly cobalt carbonate. With the extension of the reactant addition time, more needle-shaped crystals were formed, which seemed to be a double salt of cobalt carbonate hydroxide. The results obtained in the present work are consistent with the results reported by Zhang et al. (2017) and Peng et al. (2020). The longer reactant addition time meant that the precipitation mainly occurred at a relatively high pH. More cobalt carbonate hydroxide precipitated due to the higher concentration of hydroxide ions.

3.4. Effect of temperature on precipitation

Temperature is usually an important factor affecting the precipitation process. In the present work, four temperatures in the range between 40 °C and 65 °C were investigated with a reactant addition time of 400 min (feeding rate of 0.2 mL/min), aging time of 30 min, and H₂SO₄ concentration of 0.2 mol/kg. The PXRD patterns for precipitates obtained at various temperatures are shown in Fig. 3(d). It is clear that the precipitated solid was mainly cobalt carbonate. With increasing temperature, the characteristic peaks for CoCO₃ became higher and sharper, which indicates the amount of increase of crystalline CoCO3 in the precipitate. Fig. 4(j), (h), (k), and (l) show the morphology of precipitates obtained at different temperatures. The precipitated solid was made up of small, roughly spherical, single particles and their aggregates. At higher temperatures, the abundance of needle-shaped particles increased. In addition, the peaks around 15° , 18° , and 35° refer to cobalt carbonate hydrate solidification which increased at higher precipitation temperatures, as shown in Fig. 3(d). The higher temperature promotes the conversion of bicarbonate ions into carbon dioxide gas and hydroxide ions, and higher concentration of hydroxide ions enhances the precipitation of cobalt carbonate hydroxide.

3.5. Effect of mixing speed on precipitation

In this study, three mixing speeds of 300, 400, and 700 rpm were tested at 50 °C with the feeding rate of 0.5 mL/min (addition time of 160 min), aging time of 30 min, and H₂SO₄ concentration of 0.2 mol/kg. The PXRD and PSD results for products obtained from various mixing speeds are shown in Fig. 5 (a), and (b), respectively. The PXRD patterns show that the precipitated solid was cobalt carbonate. As shown in Fig. 5 (b), the average particle size decreased from 23 µm to 15 µm with the increase in rotation speed from 300 rpm to 700 rpm. However, the PSD remained the broadest at the rotation speed of 300 rpm. The precipitate obtained at 700 rpm has the greatest fraction of crystals smaller than 1 µm. This indicates that the crystals are broken to some extent due to higher mixing intensity.

3.6. Cobalt recovery and impurities in the precipitates

The cobalt recovery efficiency and the impurities observed in the crystalline products are always very important factors for evaluating precipitation processes. In order to determine the cobalt recovery efficiency and purity, chemical analyses of the precipitates obtained using various conditions were carried out, and the results are shown in Table 1. The selected impurity for the purification studies was sodium. It can be concluded that the cobalt quantity in all the precipitates was close to 49.5%, which agreed with the theoretical cobalt yield in cobalt carbonate. Based on the PXRD patterns for the precipitates, the crystalline products were mainly cobalt carbonate. The higher mass fraction of cobalt in the precipitate obtained using some conditions was probably caused by cobalt hydroxide precipitation. It also proved the validity of our assumption that it is probable that needle-like cobalt carbonate hydroxide is precipitated at higher pH, higher temperature, or with a longer reactant addition time. A comparison was made between the cobalt recovery efficiencies using various conditions, based on mass ratio between Co in crystals and Co in initial solution according to Eq. 1. The Co recovery efficiency decreased from 103% to around 91% with the increase in H₂SO₄ concentration in the initial CoSO₄ solution from 0 to 0.5 mol/kg, as shown in Table 1, while the final pH decreased from 7.2 to 6.5 as shown in Fig. 2. This is due to the fact that both precipitates (cobalt carbonate and cobalt carbonate hydroxide) are highly soluble in acidic solution. The sodium impurity in the precipitated solids was analyzed. Even though the precipitates were washed twice by rinsing with hot water, there was still sodium remained in the washed

precipitated-solid. This may be due to a small quantity of mother liquor trapped in the washed crystal cake or the adsorption of impurity on the crystal surface. In the present work, sodium impurities in the cobalt carbonate precipitates varied between 0.35 wt% and 1.12 wt%. Increasing the pH, aging time, temperature, and reactant addition time is beneficial for achieving precipitates with higher cobalt recovery efficiency and higher purity. Based on the SEM images shown in Fig. 4 and PSD analysis in Fig. 6, the degree of aggregation is the key factor affecting the product purity. The product of a higher degree of aggregation has higher impurity, which is probably due to the entrapment of mother liquor in the inclusions inside the aggregate structures.

3.7. Particle size distribution of precipitates

The particle size distribution for all the precipitates obtained under various conditions is shown in Fig. 6. It can be seen that all the precipitates have a small particle size, below $100 \ \mu\text{m}$, and the size distribution is highly related to the degree of aggregation. These results agree well with the SEM images shown in Fig. 5. As the pH decreased, the size of precipitated particles became smaller, as shown in Fig. 6(a). In Fig. 6(b), the longer aging time may have caused a decrease in the size of precipitate particles. The smallest crystals were obtained with an aging time of 180 min. For different reactant addition times (Fig. 6(c)), the particle size shows a decrease followed by an increase, as the reactant addition time varied from 160 min to 400 min and 800 min. The particles precipitated at a higher temperature were smaller in size, as shown in Fig. 6(d).

Based on the information on crystal structure obtained from the PXRD analysis shown in Fig. 3, the crystallite size was calculated using the Debye Scherrer equation (shown by Eq. (2)) (Guo et al., 2019a):

$$K_{hkl} = \frac{k\lambda}{B \bullet \cos\theta} \tag{2}$$

where K_{hkl} is the crystallite size along the [hkl] direction, in nm; k is the Scherrer constant taken to be 1; λ is the wavelength of the radiation, 1.5406Å; B is the full width at half maximum, and θ is the diffraction angle.

In this study, the calculated crystallite size of the main facets for cobalt carbonate, namely (012), (104), (110), and (113), and the average size are shown in Fig.S.2 (Supplementary material). There is no significant difference in the average crystallite size of $CoCO_3$ for different H_2SO_4 concentrations and their size is around 30 nm. This



Fig. 5. PXRD patterns (a), and PSD results for precipitates obtained from various mixing speed. (reactant addition time of 160 min (0.5 mL/min), initial H_2SO_4 concentration of 0.2 mol/kg, aging time of 30 min, and temperature of 50 °C).

Table 1

Chemical analysis results for precipitates obtained under various conditions.

No.	Precipitation conditions				Chemical analysis of precipitate		
	Molality of H ₂ SO ₄ (mol/ kg H ₂ O)	Aging time (min)	Reactant addition time (min)	Temper- ature (°C)	Co mass related to crystal mass (wt%)	Co recovery efficiency (%) (Eq. 1)	Na mass related to crystal mass (wt%)
Exp1	0				54.1	101	0.35
Exp2	0.1	30 180 360	160	50	49.3	99.9	1.04
Exp3	0.2				48.3	91.0	1.12
Exp4	0.5				48.8	91.4	1.00
Exp5					48.8	103	1.07
Exp6					48.6	99.4	0.86
Exp7			800		51.2	96.7	0.51
Exp8	0.2				48.1	94.9	1.02
Exp9		30	400	40	51.1	90.8	1.02
Exp10				60	50.6	96.0	0.86
Exp11				65	51.4	96.1	0.74

The precipitates were obtained under various conditions in a 400 mL crystallizer with a mixing speed of 400 rpm.



Fig. 6. Size distribution of precipitated particles produced under different conditions: (a) initial acid concentration (pH), (b) aging time, (c) reactant addition time, and (d) temperature (common conditions: initial H_2SO_4 concentration of 0.2 mol/kg (except in a); aging time of 30 min (except in b); reactant addition time of 160 min (except in c); temperature of 50 °C (except in d).

average size has slightly increased (30.5–35.8 nm) when extending the aging time from 30 min to 180 min. However, a further increase in the aging time to 360 min decreases the size to 32.6 nm. The reactant addition time also shows a larger effect on the average crystallite size

that increased from 30.5 nm to 44 nm as reactant addition time increased from 160 min to 400 min and then decreased to 41.5 nm at reactant addition time of 800 min. The temperature has a significant impact on crystallite size that increased from 29.8 nm to 64.8 nm as

temperature increased from 40 to 65 °C.

3.8. Investigation of precipitation process

In order to gain a better understanding of cobalt carbonate precipitation, eight suspension samples, named samples 1 to 7 and final, were studied at different pH values (10.2, 9.5, 9, 8.5, 8, 7, and 6.7) during precipitation and at the end of the experiment under the conditions maintained at 0.2 mol/kg H₂SO₄, reactant addition time of 400 min (feed rate of 0.2 mL/min), temperature of 50 °C, and aging time of 30 min. The mother liquor and precipitate were separated and analyzed as explained in Section 2.2. The FBRM was applied for real-time monitoring of the particles count of various chord length fractions, and the pH was measured continuously throughout the precipitation process.

The count rates obtained by FBRM and the pH changes during precipitation are presented in Fig. 7. The asterisk denotes the starting point of reactant addition and the diamond symbol denotes the end point. Samples 1 to 7 are the times of sample collection, as shown in Fig. 7. It can be seen from the pH curve how the pH decreased during the feeding of cobalt sulfate solution. Before feeding, solid sodium carbonate was dissolved in water, resulting in an alkaline solution. The dissolution of sodium carbonate was assumed to occur according to Eqs. (3) and (4). At the beginning of feeding, the pH shows a significant drop, which may be attributed to the neutralization of free H^+ and OH^- , as in Eq. (5), and the cobalt carbonate hydroxide precipitation as in Eqs. (11) and (12). The decrease in pH slowed down in the final feeding time period of acidic cobalt sulfate solution. In this period, the main reaction could be the conversion from carbonate to bicarbonate and even carbonic acid, according to Eqs. (6) and (7). In addition, as the precipitation temperature was 50 °C, the decomposition of carbonic acid or bicarbonate, which releases carbon dioxide according to Eqs. (8) and (9), could have occurred during the precipitation. The Raman spectrum and the quantified ion concentration using the Raman calibration models are shown in Fig. 8. It is clear that the concentration of carbonate ions decreased when the pH value decreased and approached zero at pH values lower than 7. The bicarbonate ion concentration first increased and then decreased. The highest bicarbonate concentration was found for sample 4 with a pH value of 8.5. The carbon species distribution with various pH values agrees well with the ionic species distribution diagram reported by Shim et al. (2016). As expected, the sulfate ion concentration corresponding to the amount of cobalt sulfate solution added increased at a constant rate.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-} \tag{3}$$

$$CO_3^{2-} + H_2 O \rightleftharpoons HCO_3^{-} + OH^{-} \tag{4}$$

$$OH^- + H^+ \rightleftharpoons H_2 O \tag{5}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{6}$$

$$HCO_3^- + H^+ \to H_2CO_3 \tag{7}$$

$$H_2CO_3 \rightarrow H_2O + CO_2 \tag{8}$$

$$HCO_3^- \to CO_2 + OH^- \tag{9}$$

Based on the FBRM results, the precipitation occurred once feeding started. The increase in the count rates of various chord length fractions was slow at pH values above 8.5 (sample 4). At pH values lower than 8.5, the count rates started to increase significantly. When the pH approached the value of 7, the count rates for a chord length smaller than 10 µm became constant and the count rates for a chord length at 10 to 100 µm increased slightly. It was assumed that the count rate changes in the chord length fraction smaller than 10 um corresponded mainly to the nucleation rate, whereas the crystal growth rate was associated with the count rate changes occurring in the chord length fraction between 10 and 100 µm. Based on this approach, the nucleation rate became very low and the particle growth continued after the pH decreased to 7. The PXRD patterns for samples 2-7 and the final precipitate are shown in Fig. 9. It was found that the main solid phase for sample 2 was cobalt carbonate hydroxide. With a continuous decrease in pH, the characteristic peaks for cobalt carbonate were detected. Samples 3 to 5 were also identified as cobalt carbonate hydroxide. As the pH decreased down to



Fig. 7. Count rates obtained by FBRM and pH trends over time at H_2SO_4 concentration of 2 mol/kg, reactant addition time of 400 min (feed rate of 0.2 mL/min), temperature of 50 °C, and aging time of 30 min.



Fig. 8. Raman analysis of mother liquor samples obtained at various pH values during the precipitation process: (a) Raman spectrum; (b) concentration of anions quantified via Raman calibration models. (H₂SO₄ concentration of 2 mol/kg, reactant addition time of 400 min (feed rate of 0.2 mL/min), temperature of 50 °C, and aging time of 30 min; numbers refer to Fig. 7).



Fig. 9. PXRD patterns for solid samples collected from the precipitation process. (H_2SO_4 concentration of 2 mol/kg, reactant addition time of 400 min (feed rate of 0.2 mL/min), temperature of 50 °C, and aging time of 30 min; numbers refer to Figs. 7 and 8).

7, cobalt mainly precipitated as cobalt carbonate. The crystallinity of the precipitate increased in the final period of evolved time. Based on the PXRD patterns for samples 6 and 7, and final, the crystallite size for the main facets were estimated to investigate the cobalt carbonate crystal growth, as shown in Fig.S.3 of the supplementary material. Among these crystal planes, the crystal size of the (012) facet orientation decreased as the precipitation proceeded. Instead, the other three facet orientations (104), (110), and (113) presented gradual growth states. These crystallite sizes reflected the degree of growth of the corresponding facet orientations. In this precipitation process, cobalt carbonate mainly grew along orientations (104), (110), and (113).

The results obtained by pH, FBRM, Raman analysis of anionic compositions, and PXRD analysis prove that cobalt carbonate hydroxide precipitated at pH values higher than 9. With cobalt sulfate feeding and the continuous decrease in pH, more cobalt carbonate precipitated at lower pH (around 8–9), and final cobalt precipitated as cobalt carbonate at pH lower than 7. The reactions that occurred are shown as Eqs. (10), (11), and (12). The results show a good agreement with *E*-pH diagram of Co-C-H₂O system (Fig. S4) where cobalt hydroxide is stable at higher pH and cobalt carbonate is stable at lower pH.

$$Co^{2+} + CO_3^{2-} \rightarrow CoCO_3(s) \tag{10}$$

$$2Co^{2+} + CO_3^{2-} + 2OH^- \to Co_2(CO_3)(OH)_2(s)$$
(11)

$$Co^{2+} + 2OH^{-} \rightarrow Co(OH)_2(s) \tag{12}$$

The SEM images for samples shown in Fig. 10 also reveal that the proposed precipitation reactions are valid. The particles first precipitated as large aggregates formed of single needle-shaped particles, as shown in Fig. 10(a). Based on the PXRD pattern obtained, these elongated needle-shaped particles are cobalt carbonate hydroxide. As precipitation continues, there is a mixture of needle-shaped double salt and cobalt carbonate aggregates formed of spherical single crystals. The quantity of spherical particles increases with the feeding of cobalt sulfate solution, as can be seen from Fig. 10(b)-(g). At the end of precipitation, most of the precipitated particles are spherical single crystals and



Fig. 10. SEM images for solid samples collected from the precipitation process: (a)-(h) refer to samples 1-7 and the final precipitate, respectively. (H₂SO₄ concentration of 0.2 mol/kg, reactant addition time of 400 min (feed rate of 0.2 mL/min), temperature of 50 °C, and aging time of 30 min.)

their aggregates, which were identified as cobalt carbonate by PXRD.

4. Conclusions

The precipitation of cobalt carbonate was investigated by feeding pure or acidic aqueous cobalt sulfate solution into aqueous sodium carbonate solution. The reactant addition time, aging time, mixing speed, and temperature also affected the cobalt recovery efficiency, impurity in the precipitates, and properties of precipitated particles such as the main solid forms, crystallinity, morphology, and particle size distribution. Based on the findings from this work, the recommendations for the optimal conditions to recover cobalt carbonate as follows: initial cobalt(II) sulfate solution of 2 mol CoSO₄/kg water and 0.2 mol H₂SO₄/kg water, initial sodium carbonate solution of 1 mol/kg water, temperature of 50 °C, aging time of 30 min, and reactant addition time of 400 min.

In the present work the anionic composition of carbonates and sulfates in the mother liquor were determined. Raman analysis proved to be a suitable tool for quantification of dissociated univalent and divalent anions in addition to solid form analysis. Based on the Raman results obtained, it was concluded that Raman spectrometry has great potential to be applied as an advanced monitoring and control tool for the recovery of critical metals by precipitation.

The pH proved to have a significant impact on cobalt carbonate precipitation. When feeding acidic cobalt sulfate solution, the pH of the suspension decreased, and cobalt precipitated in different solid forms depending upon the pH range. In the pH range between 9 and 11, cobalt carbonate hydroxide was the main precipitate. When the pH continuously decreased to a pH range between 8 and 9, cobalt carbonate started to precipitate. When pH reached the value of 7, cobalt carbonate became the main product in the precipitated solid.

The tendency for aggregation during cobalt carbonate precipitation has an influence on the inclusion of impurities in precipitates. It was concluded that the crystal purity can be affected by two factors: heavy aggregation tendency may cause the entrapment of the mother liquor in product crystals and also the impurities can be adsorbed on the surface of small particles. Therefore, decreasing the aggregation tendency in cobalt carbonate precipitation may yield higher crystal purity.

CRediT authorship contribution statement

Jianxin Zhang: Conceptualization, Investigation, Formal analysis, Visualization, Writing – original draft, Methodology, Validation, Writing – review & editing. **Rajaboopathi Mani:** Writing – review & editing, Supervision. **Marjatta Louhi-Kultanen:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

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