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Use of manganese sulfide as a sustainable precipitant for the separation of Co(II) and Ni(II) by sulfide precipitation from spent lithium-ion battery leachates

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Abstract: The rising uptake for lithium-ion batteries (LIBs) requires the need for effective recycling methods to recycle critical metals like cobalt, nickel, and manganese while minimizing environmental harm. In general, hydrometallurgical treatments of spent LIBs result in leachates that contain Co(II), Mn(II) and Ni(II) with diverse concentration ratio. By utilizing the difference in the solubility products among CoS, NiS and MnS, it is possible to simultaneously precipitate CoS and NiS, leaving Mn(II) in the filtrate. This study employed MnS as a cost-effective and eco-friendly precipitant for selective precipitation of Co(II) and Ni(II) sulfide from simulated solution containing Mn(II). Among several factors, the influence of solution pH, MnS dosage and reaction time was found critical on the precipitation of Co(II) and Ni(II) at room temperature. Under optimized conditions: pH 2.0, a MnS/(Co + Ni) molar ratio of 10, agitation speed of 400 rpm at 25℃, use of MnS led to complete precipitation of CoS and NiS, leaving Mn(II) in the filtrate with minimal contamination. Moreover, common ion effect and encapsulation effect were observed to affect the dissolution behavior of MnS during the precipitation. Unlike traditional sulfide sources like Na_2S and NaHS, MnS provides a controlled release of sulfide ions, addressing challenges like the formation of colloidal particle. Our results indicated that MnS demonstrated its potential as a precipitant for the selective precipitation of Co(II) and Ni(II) from the acidic media containing Mn(II).

Keywords: sulfide precipitation, MnS, cobalt, nickel, separation

1. Introduction

Lithium-ion batteries (LIBs) have become indispensable in up-to-date energy technology due to exceptional features, such as high specific density, compact design, good durability (over 1,000 cycles), fast charging, low discharge rate, and reliable performance (Duan et al., 2020; Nguyen et al., 2022). These advantages make LIBs essential for many applications, including consumer electronics, industrial systems, grid energy storage, and electric vehicles. Especially, LIBs could power a wide range of electric vehicles, contributing to reduced emissions and global climate targets through high energy efficiency and cost-effectiveness (Yu et al., 2018; Duan et al., 2020). Despite these benefits, the increasing use of LIBs has caused shortages of essential metals of LIBs like lithium, cobalt, and nickel, which are key components to their production (Ordoñez et al., 2016; Zheng et al., 2018). The accumulation of end-of-life LIBs poses threats to human health and the environmental impacts due to the release of metal overload and toxic electrolytes if improperly disposed (Liu et al., 2019). These issues highlight the urgent need for recycling of valuable materials in order to reduce environmental harm and to make LIB technology sustainable for the future (Chitre et al., 2020; Chen et al., 2024; Wen et al., 2024).

Therefore, a circular economy approach is becoming essential. Among diverse recycling methods for the retrieval of valuable metals (He et al., 2017; Asadi Dalini et al., 2021; Eray, 2023; Wang et al., 2023), hydrometallurgy is indispensable in isolating the metal ions with comparable chemical characteristics from the leaching solution of secondary resources (Tran and Lee, 2022; Zhao et al., 2024). In general, the leaching solutions of secondary resources contain diverse kinds of metal ions, making it difficult to

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separate and recover individual elements. In most of the hydrometallurgical processes of spent LIBs, other base metal ions except for Co(II), Mn(II) and Ni(II) are selectively isolated through some operational techniques such as cementation, reduction, precipitation, ion exchange, and solvent extraction (Wang et al., 2019; Djoudi et al., 2021; Saneie et al., 2022; Tran et al., 2022). Specifically, in the hydrometallurgical recycling of LIB leachates containing Al(III), Fe(III), Cu(II), Mn(II), Co(II), Ni(II) and Li(I), Al(III), Fe(III) and Cu(II) are isolated before the separation of Co(II), Mn(II), Ni(II) and Li(I). First, copper ion is removed by iron reduction. Subsequently, iron and aluminium ions are precipitated as $Fe(OH)_3$ and $Al(OH)_3$. The remaining manganese can then be extracted using solvents like D2EHPA, leaving cobalt, nickel, and lithium in the raffinate (Peng et al., 2020). Among the various separation techniques, selective precipitation and solvent extraction are widely applied. For instance, precipitants such as dimethylglyoxime and ammonium oxalate, along with extractants like D2EHPA, can be used to separate these metal ions (Chen and Zhou, 2014). Alternatively, sodium carbonate has also demonstrated potential for the consecutive separation of Mn(II), Ni(II), and Li(I) (Meshram et al., 2015).

Solvent extraction offers high selectivity for target metal ions even with low concentrations, and is well-suited to continuous operation. Despite these advantages, it relies on costly organic reagents, posing environmental risks due to volatile solvents, and demands stringent control to minimize losses and cross-contamination (Kang et al., 2010; Pranolo et al., 2010; Zhao et al., 2011; Nguyen and Lee, 2021). On the other hand, precipitation is cost-effective, simple, and allows selective metal recovery based on the difference in solubility, making it appropriate for bulk recovery. It is particularly effective for treating complex solutions and producing stable residues suitable for further processing. However, it may generate colloidal particles, require precise control to avoid contamination, and involve high reagent consumption, especially with soluble sulfur sources (Wang et al., 2009; Chen et al., 2015; Ho et al., 2024; Wen et al., 2024). The key challenge in hydrometallurgical recycling of spent LIBs lies in the efficient separation of cobalt, nickel, and manganese ions from each other. These three metal ions share very similar chemical behavior, particularly in their divalent states. Various solvent extraction procedures are reported on the separation of Co(II), Mn(II) and Ni(II) from either sulfate or chloride solution (Li et al., 2018; Zhou et al., 2021; Jeon et al., 2024). Generally, the presence of Mn(II) species in leachates complicates the separation of Co(II) and Ni(II) by solvent extraction. This is because most extractants designed for the separation Co(II) and Ni(II) also show a significant affinity for Mn(II), leading to co-extraction and poor purity. By utilizing the diverse oxidation state of manganese ion and its high oxidation potential, Mn(II) is often separated by oxidative precipitation of MnO_2 (Tran et al., 2022; Wen et al., 2024).

Among several precipitation methods, sulfide precipitation is employed for metal recycling due to its simplicity, cost-effective, and good selectivity on the basis of differences in solubility (Zhang et al., 2023). This solubility difference presents a promising avenue to directly tackle the separation of Co(II), Ni(II) and Mn(II). Traditional soluble sulfur sources such as soluble sulfur-based compounds such as Na_2S and NaHS are effective precipitants, with studies showing their ability to achieve high recoveries of Co(II) and Ni(II) with exceptional purity (Ho et al., 2024). For instance, Na_2S has been employed to selectively co-precipitate Co(II) and Ni(II) while retaining Mn(II) in solution (Ho et al., 2024), and Zn(II), Co(II), and Mn(II) are successfully eliminated at specific pH ranges by Na_2S, with reported recoveries of 93.45%, 95.15%, and 100% at pH 2, 3, and 8 for Zn(II), Co(II), and Mn(II), respectively (Fattahi et al., 2016). However, these reagents often result in challenges, such as local super-saturation of sulfide ions, colloidal particle formation, and high reagent consumption (Zhang et al., 2023). To overcome these limitations, researchers have investigated insoluble sulfur-based compounds like CaS, FeS, and MnS, which offer enhanced control over the release of sulfide ion and improved performance in acidic conditions (Gharabaghi et al., 2012; Li et al., 2014; Luo et al., 2022; Yang et al., 2022). Among these, manganese sulfide stands out for its stable dissolution behavior in acidic environments, providing a reliable in-situ source of sulfide ions. These characteristics make MnS an excellent candidate for treating LIBs leachates consisting of Co(II), Ni(II), and Mn(II). Unlike traditional sulfur sources, MnS avoids introducing impurities, maintaining solution purity for downstream processing. Through pH control and optimization of MnS dosage, MnS enables selective precipitation of Co(II) and Ni(II), leaving Mn(II) in solution. This study aimed to examine the potential use of MnS as a sustainable and efficient sulfur source for LIB recycling, with a focus on meeting the growing need for eco-friendly metal recovery methods. By investigating key factors such as pH, MnS dosage, concentration ratio of the metal ions and reaction time, the separation of Co(II) and Ni(II) by sulfide precipitation with MnS was investigated. This innovative approach supports a circular economy and promotes sustainable practices for metal recovery, paving the way for a greener future.

2. Materials and methods

2.1. Reagent and chemicals

The synthetic solutions containing Co(II), Mn(II), and Ni(II) were prepared by dissolving a definite amount of the metal sulfates, such as cobalt(II) sulfate ($CoSO_4 \cdot 7H_2O$, Junsei Co., 98%), manganese(II) sulfate ($MnSO_4 \cdot nH_2O$, Duksan Co., 98.5%) and nickel(II) sulfate ($NiSO_4$, Daejung Co., 98.5%) in doubly distilled water. In most of the experiments, the initial concentration of the metal ions in the synthetic solutions was fixed at 1000 mg/L. The pH values of the synthetic solutions were adjusted by adding sulfuric acid solution (H_2SO_4, Daejung Co., 95%) or sodium hydroxide (NaOH, Duksan Co., >99%). Manganese sulfide (MnS, Thermoscientific Co., 99.9%) was employed as a precipitant. All chemicals employed in this work were used without any further purification.

2.2. Procedure and analytical methods

In the precipitation experiments, the precipitant was added to a 20 mL of the solution using a 100 mL glass beaker with a cover. The reaction parameters, such as stirring speed, reaction time and temperature, were controlled by using a magnetic stirrer (WiseStir MSH-20D, Daihan Scientific Co., Korea). The solid residues and the filtrate after precipitation experiments were separated by using filter paper (ADVANTEC No. 2, 110 mm, Toyo Roshi Kaisha, Ltd). The concentrations of the metal ions in the solutions were measured by using inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Germany). The pH values of the solutions were determined by a pH meter (Orion Star A211, Thermo Scientific, USA). The precipitation percentage (%) of the metal ions was calculated as $\%P = (m_{initial} - m_{filtrate})/m_{initial} \times 100\%$, where $m_{initial}$ and $m_{filtrate}$ are the mass of the metal ions in the solutions before and after precipitation experiments.

3. Results and discussion

3.1. The effect of the molar ratio of MnS

Co(II) and Ni(II) exhibit similar chemical properties, such as ionic radii, standard reduction potentials, and coordination chemistry, which hinders their effective separation. Meanwhile, there is some difference in the chemical properties between Mn(II) and Co(II)/Ni(II). Unlike Co(II) and Ni(II), manganese ions can exist in multiple oxidation states, including Mn(II), Mn(III), Mn(IV), Mn(VI), and Mn(VII). According to the hard and soft acid–base (HSAB) principle, the sulfide ion is classified as a soft base and therefore exhibits a strong affinity for soft acids. Co(II) and Ni(II), being softer acids than Mn(II) (James, 2017) tend to interact more strongly with sulfide ions compared to Mn(II). Therefore, CoS and NiS exhibit significantly lower solubility compared to MnS, which is reflected by the values of their solubility products for the three correspoding metal sulfides as listed in Table 1 (James, 2017). Taking advantage of the difference in solubility, it becomes feasible to simultaneously isolate Co(II) and Ni(II) away from Mn(II) through introducing MnS as a source of sulfide ion for the precipitation. In general, Na_2S or NaHS is employed for the precipitation of CoS and NiS (Liu et al., 2017; Ho et al., 2024). However, the employment of Na_2S or NaHS introduces sodium ions into the solution. By contrast, use of MnS as a precipitant would reduce the contamination of Mn(II) solution by introducing impurity ions, resulting in a favourable effect on the purification process of pure Mn(II) species from the resulting solutions.

Table 1. The solubility product (Ksp) values of CoS, NiS and MnS at 25℃ (James, 2017).

Metal sulfide	Ksp
CoS	5.01×10^{-22}
NiS	3.98×10^{-20}
MnS	3.16×10^{-11}

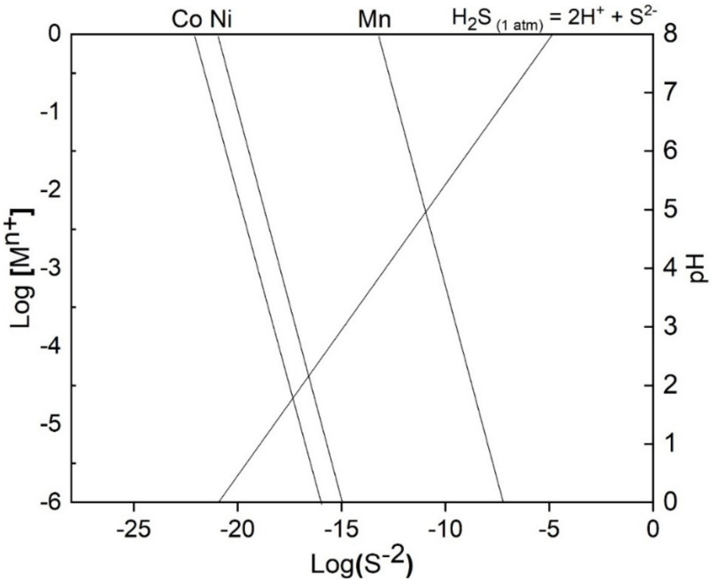

Fig. 1. Sulfide solubility diagram of Co(II), Mn(II) and Ni(II) ions at 25 ℃ (Zhang and Cheng, 2007).

Fig. 1 is a sulfide solubility diagram for CoS, NiS and MnS at 25°C for a solution saturated with gaseous H_2S (Zhang et al., 2023). From this figure, the equilibrium concentration of sulfide ion at a specific solution pH can be read from the interception between the specific pH and sulfide concentration. Moreover, the equilibrium concentration of a metal ion at this solution pH is found from the intersection of the line between the metal sulfide and the concentration of sulfide ion.

According to Fig. 1, the equilibrium concentration of Co(II) and Ni(II) would be less than 10^{-4} M at a solution pH of 2. The precipitation pH of metal sulfides can be determined from the solubility product values by using the following reaction (Bard et al., 1985).

$$2H^+ + S^{2-} = H_2S_{(g)},\ K_{298} = 9.1\times10^{18} \quad (1)$$

$$CoS = Co^{2+} + S^{2-} \quad (2)$$

$$NiS = Ni^{2+} + S^{2-} \quad (3)$$

$$MnS = Mn^{2+} + S^{2-} \quad (4)$$

When the concentrations of the three metallic ions in the mixture are 1 g/L, the precipitation pH of CoS, NiS and MnS would be -0.28, 0.66, and 5.10, respectively. Due to the significant difference in the pH values required for the precipitation of Mn(II) compared to Co(II)/Ni(II), the selective separation of Co(II) and Ni(II) from Mn(II) can be accomplished by carefully controlling solution pH and the dosage of MnS. The above calculation results indicate that solution pH needs to be controlled between the precipitation thresholds of NiS and MnS.

In order to examine how varying amounts of MnS influence the precipitation behavior, the molar ratio of MnS to the sum of Co(II) and Ni(II) was changed from 1 to 10, while maintaining solution pH at 2.0. These experiments were performed at ambient temperature for 30 minutes with constant stirring at 400 rpm. The precipitation behavior of Co(II) and Ni(II) with the molar ratio of MnS/(Co(II)+Ni(II)) is shown in Fig. 2, along with the corresponding changes in Mn(II) concentration in the mixture. According to the data, the precipitation percentages of Co(II) and Ni(II) increased significantly as the molar ratio of MnS/(Co(II)+Ni(II)) increased from 1 to 10. At a molar ratio of 1, the removal rates of Co(II) and Ni(II) were 28.8% and 26.7%, respectively, with Mn(II) species remaining at 2,343 mg/L. As the ratio increased to 7, the precipitation percentages increased to 99.2% and 92.4%, respectively, with a corresponding Mn(II) concentration of 9,039 mg/L. Complete co-precipitation of Co(II) and Ni(II) was achieved at a molar ratio of 10, leaving the Mn(II) concentration at 9,566 mg/L.

3.2. The effect of pH

The impact of solution pH on the precipitation of Co(II) and Ni(II) was studied by adjusting solution pH between 2.0 and 5.0, while maintaining a constant molar ratio of MnS to (Co(II)+Ni(II)) at 10. In these

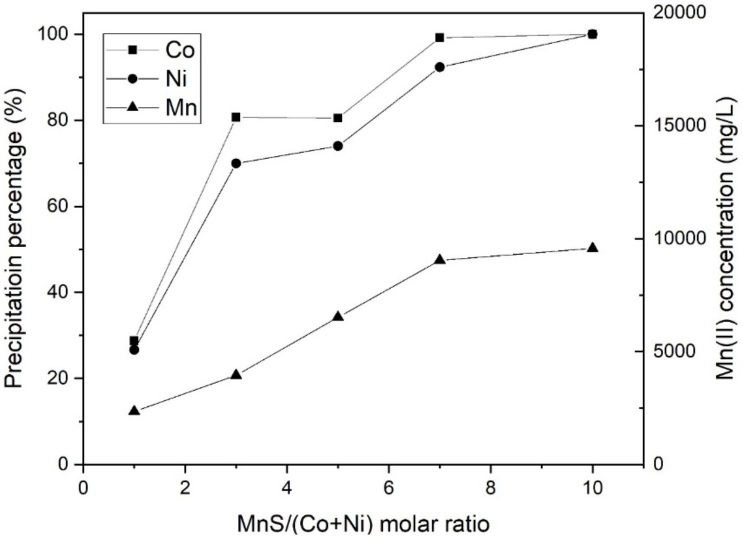

Fig. 2. The effect of the molar ratio of MnS to the sum of Co(II) and Ni(II) on the precipitation of Co(II) and Ni(II) and on the change in the concentration of Mn(II) in the filtrate. (Condition: initial concentrations of the Co(II), Ni(II), Mn(II) : 1000 mg/L, pH = 2.0, 30 mins, 400 rpm, room temperature.)

these experiments, other conditions were maintained at the same as those in Sec. 3.1, namely, reaction time of 30 minutes, agitation speed of 400 rpm, and room temperature. Fig. 3 highlighted a critical role of solution pH in influencing the dissolution of MnS and the subsequent precipitation of CoS and NiS. At pH 2.0, complete precipitation of Co(II) and Ni(II) was observed, while Mn(II) remained primarily in solution at a level of 9,373 mg/L. This indicates that MnS dissolves effectively at low pH, liberating sufficient sulfide ions to precipitate CoS and NiS. When solution pH is 2, some of the dissolved sulfide ions can be protonated to HS^-. However, the results obtained at pH 2.0 confirmed that the concentration of sulfide ions present in solution was adequate to completely precipitate Co(II) and Ni(II).

When solution pH was raised to 3.0, complete precipitation of Co(II) was achieved, while the precipitation efficiency of Ni(II) declined slightly to 96.7%, with the corresponding decrease in the Mn(II) concentration to 8,073 mg/L. However, when the pH exceeded 3, that of Co(II) and Ni(II) dropped significantly. At pH 4.0, only 30.3% of Co(II) and 27.0% of Ni(II) were precipitated, with the concentration of Mn(II) decreasing further to 1,986 mg/L. At pH 5.0, the precipitation percentages of Co(II) and Ni(II) fell to 23.5% and 22.5%, respectively, while Mn(II) concentration decreased to 1,634 mg/L.

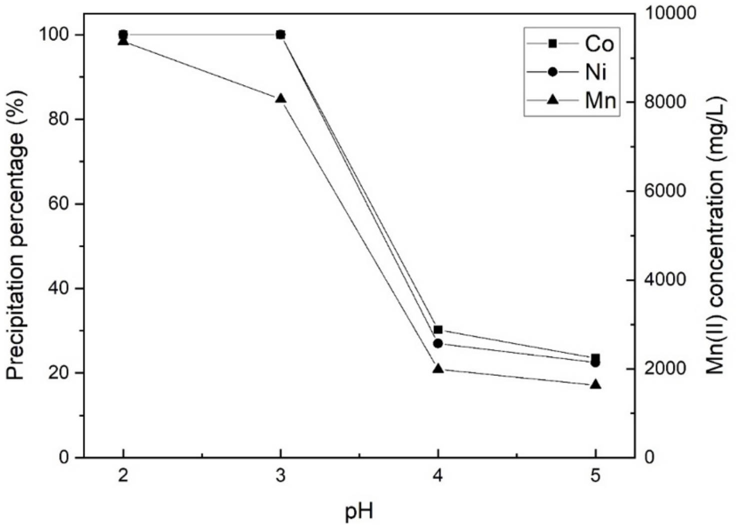

Fig. 3. The effect of solution pH on the precipitation of Co(II) and Ni(II) and on the change in the concentration of Mn(II). (Condition: initial concentrations of the Co(II), Ni(II), Mn(II): 1000 mg/L, molar ratio of MnS/(Co(II)+Ni(II)) :10, 30mins, 400 rpm, room temperature.)

The variation in Mn(II) concentration indicated that the dissolution degree of MnS rapidly dropped as solution pH increased from 2.0 to 5.0. In this set of experiments, the molar ratio of MnS/(Co(II)+Ni(II)) was kept constant at 10. This decrease in Mn(II) concentration can be ascribed to the common ion effect (Ayogu et al., 2020). According to Fig. 1, the concentration of sulfide ion is proportional to solution pH. Therefore, as solution pH increases, there would be more sulfide ion, which suppress the dissolution of MnS due to common ion effect. In these circumstances, the precipitation efficiency of Co(II) and Ni(II) would be reduced owing to an insufficient amount of sulfide ion which is required for the precipitation reaction. Our findings clearly demonstrated that maintaining solution pH at 2 or below is essential to promote effective MnS dissolution and subsequent co-precipitation of CoS and NiS.

3.3. The effect of reaction time

Reaction time was adjusted between 1 and 45 minutes to evaluate its effect on the precipitation of Co(II) and Ni(II). The operating conditions were conducted in accordance with the following conditions: MnS/(Co(II)+Ni(II)) molar ratio of 10, pH 2.0, room temperature, and agitation at 400 rpm. As depicted in Fig. 4, increasing reaction time led to enhanced precipitation, with Co(II) rising from 55.7% to 99.9% and Ni(II) from 47.5% to 99.9% as the duration was extended to 30 minutes. Beyond 30 minutes, the precipitation percentages remained constant, indicating that equilibrium had been reached. These results indicated that the precipitation reaction can be finished within 30 minutes under the given experimental conditions.

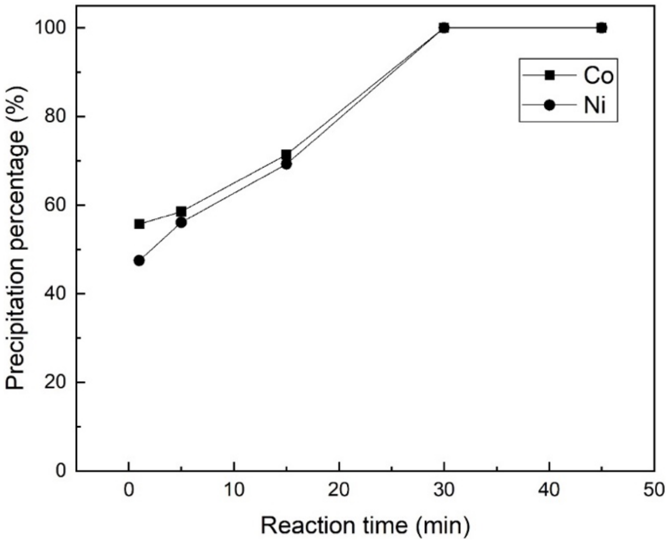

Fig. 4. The effect of reaction time on the precipitation of Co(II) and Ni(II) from the solution with pH 2.0. (Condition: initial concentrations of the Co(II), Ni(II), Mn(II) : 1000 mg/L, molar ratio of MnS/(Co(II)+Ni(II)) of 10, 400 rpm, room temperature.)

To assess the influence of the presence of Co(II) and Ni(II) on the dissolution kinetics of MnS, another experiment was done using pure Mn(II) solution with 1000 mg/L concentration. In Fig. 5, change in Mn(II) concentration was compared between pure Mn(II) solution and the mixed solution containing the three metal ions with 1000 mg/L concentration. There was not much difference in the dissolution kinetics of MnS between the two kinds of solutions. Significant dissolution of MnS occurred during the initial 15 minutes, as evidenced by the rapid rise in the Mn(II) concentration from 5,992 mg/L at 1 minute to 9,996 mg/L at 15 minutes. After 30 minutes, the Mn(II) concentration remained nearly unchanged, indicating that MnS dissolution reached a steady state. These results indicate that not only MnS dosage and solution pH but also reaction time is important to selectively co-precipitate Co(II) and Ni(II) over Mn(II). Moreover, the presence of Co(II) and Ni(II) did not affect the dissolution of MnS as long as solution pH was maintained at 2. As a result, subsequent experiments were conducted at a reaction time of 30 minutes to enable complete precipitation of Co(II) and Ni(II) under suitable conditions.

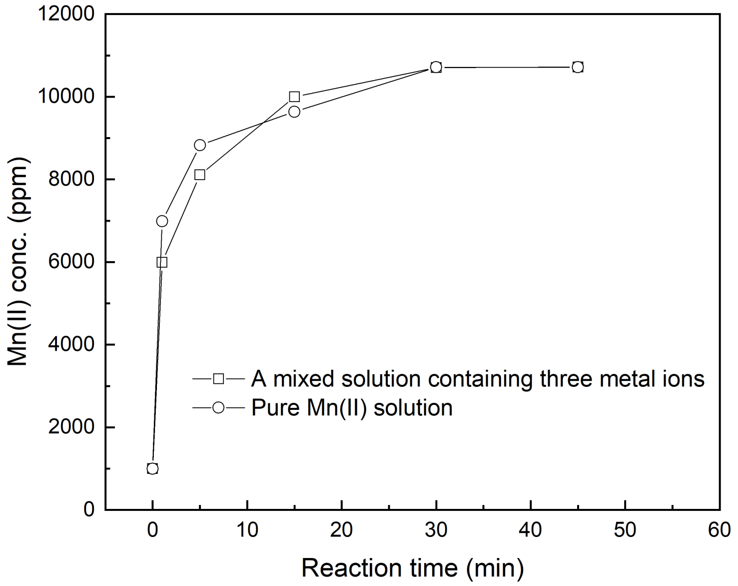

Fig. 5. Comparison of the effect of reaction time on the change in the concentration of Mn(II) owing to dissolution between the solution containing the three metal ions and pure Mn(II) solution. (Condition: initial concentrations of the Co(II), Ni(II), Mn(II) in the mixed solution: 1000 mg/L, the concentration of Mn(II) in pure Mn(II) solution :1000 mg/L, molar ratio of Mn/(Co(II)+Ni(II)) of 10, pH 2.0, 400 rpm, room temperature.

3.4. The effect of metal concentration ratio

In dissolving sparingly soluble substances, common ion effect is important. The concentration ratio of Co(II)/Ni(II) to Mn(II) would affect the precipitation behaviour of CoS and NiS by using MnS as a precipitant. Therefore, further experiments were performed by varying the concentration ratio of Co(II)/Ni(II) to Mn(II) from the mixture with pH 2.0. For this purpose, Mn(II) concentration was fixed at 1000 mg/L, while that of Co(II)/Ni(II) was varied from 100 mg/L to 10,000 mg/L. According to Fig. 6, when the concentrations of Co(II) and Ni(II) were lower than Mn(II) species, such as 100 and 500 mg/L, incomplete precipitation of Co(II) and Ni(II) occured. In these conditions, the precipitation percentages of Co(II) (76.9% and 81.9%) were higher than those of Ni(II) (52.5% and 67.5%) due to smaller solubility product of CoS than NiS. Considering the precipitation pH of MnS, there should be enough sulfide ions in solution with pH 2 which can take part in the precipitation reaction, when the molar ratio of MnS to the sum of Co(II) and Ni(II) was 10. However, Co(II) and Ni(II) were not completely removed as long as their concentrations were less than 1000 mg/L. This behavior is related to common ion effect and can be explained on the basis of thermodynamics and kinetics. First, the change in Gibbs free energy, ΔG associated with the precipitation of CoS can be given by

$$Co^{2+} + S^{2-} = CoS_{(s)},\ K = 1/K_{SP} \tag{5}$$

$$\Delta G = \Delta G^{\circ} + RT\ln Q \tag{6}$$

where ΔG° denotes the standard Gibbs free energy change of the precipitation reaction. In Eq. (6), the reaction quotient (Q) is related to the initial concentration of the species. Therefore, Eq. (6) for the precipitation of CoS can be represented as

$$\Delta G = \ln \frac{K_{SP}}{[Co^{2+}][S^{2-}]} \tag{7}$$

Eq. (7) indicates that the Gibbs free energy change for the precipitation reaction would be decreased with a rise in the concentration of Co(II), when the sulfide ion concentration is constant. Our results were in good agreement with thermodynamic prediction. Second, from the kinetic point of view, precipitation occurs through nucleation and growth of the nuclei. In general, super-saturation degree of a target metal ion has a great effect on the kinetics of both nucleation and growth. The super-saturation degree of a metal ion would be reduced as its concentration decreases. Therefore, the precipitation extent of both Co(II) and Ni(II) was decreased as their concentrations in the solution decreased.

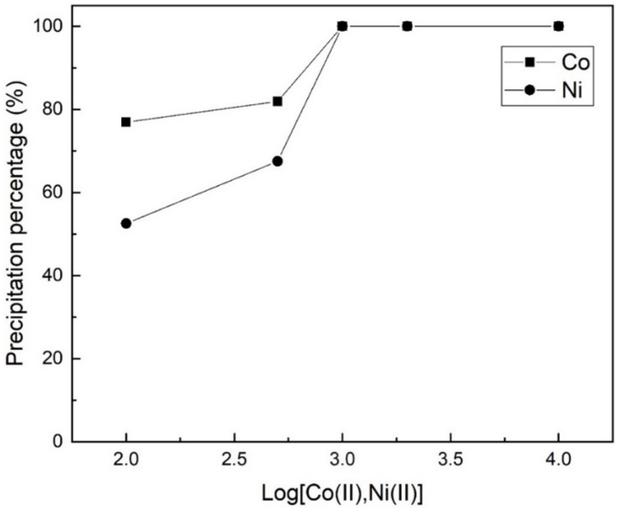

Fig. 6. The effect of the concentration of Co(II) and Ni(II) on the precipitaion at a molar ratio of MnS/(Co(II)+Ni(II)) of 10 from the solution with pH 2.0. (Condition: Mn(II) concentration was fixed at 1000 mg/L, 30 mins, and room temperature)

Further investigations were carried out by adjusting the concentration of Mn(II) in the mixture, while keeping Co(II) and Ni(II) concentrations at 1000 mg/L. In these set of experiments, the pH index was set at 2.0 and the molar ratio of MnS to the total amount of Co(II) and Ni(II) was maintained at 10. All experiments were done for 30 mins at room temperature. Fig. 7 reveals the initial concentration of Mn(II) affected the precipitation of Co(II) and Ni(II). When the initial concentrations of Mn(II) were 500 mg/L and 1000mg/L, Co(II) and Ni(II) were completely precipitated. By contrast, the precipitation percentages of Co(II) and Ni(II) were only 90% and 75% when the initial Mn(II) concentration was reduced to 100 mg/L. When MnS is introduced into a solution containing Mn(II), the solubility of MnS depends on the concentration of Mn(II) owing to common ion effect. Therefore, the solubility of MnS would be decreased with the increase in the initial concentration of Mn(II). In this case, the supply of the sulfide ion from the dissolution of MnS would control the precipitation reaction. By contrast, the concentration of sulfide ion from the dissolution of MnS would be increased as the concentration of Mn(II) decreases, resulting in rapid occurrence of the precipitation onto the surface of the MnS particles. In this case, the precipitates of CoS and MnS would cover the surface of the MnS, preventing dissolution of MnS. In this case, the precipitation percentage of CoS and NiS would be reduced owing to this "encapsulation effect" (Balasubramani et al., 2015; Rajabi et al., 2015; Baysan et al., 2021).

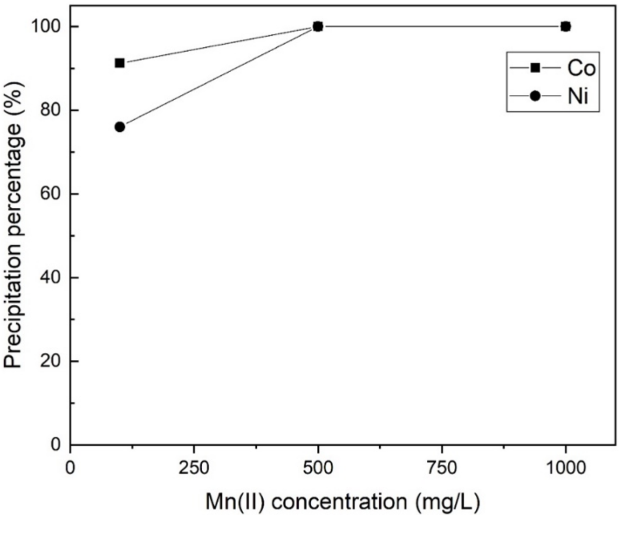

Fig. 7. The effect of Mn(II) concentration on the precipitation of Co(II) and Ni(II) at a molar ratio of MnS/(Co(II)+Ni(II)) of 10 from the solution with pH 2.0. (Condition: the concentration of Co(II) and Ni(II) : 1000 mg/L, 30min, room temperature)

XRD pattern of the residues after filtration under the optimized condition is shown in Fig. 8. The diffraction signals observed at 2θ values of 34.3°, 46.8°, and 54.2° are indexed to CoS, consistent with the reported data (Kochuparampil et al., 2017; Miao et al., 2020). Peaks corresponding to NiS were observed at 30.63° and 35.17° (Luo et al., 2017). Additionally, characteristic diffraction peaks of MnS were detected at 29.67°, 34.3°, 49.3°, 61.4°, and 72.3°, which agreed with the reported data (Mi et al., 2014). The presence of MnS in the XRD pattern suggests incomplete dissolution under the conditions. The MnS peaks, particularly those at 34.3° and 49.3°, are prominent, indicating the retention of crystalline MnS phases. In contrast, the CoS and NiS phases exhibit sharper and more intense peaks, suggesting better crystallinity and successful formation under the given conditions.

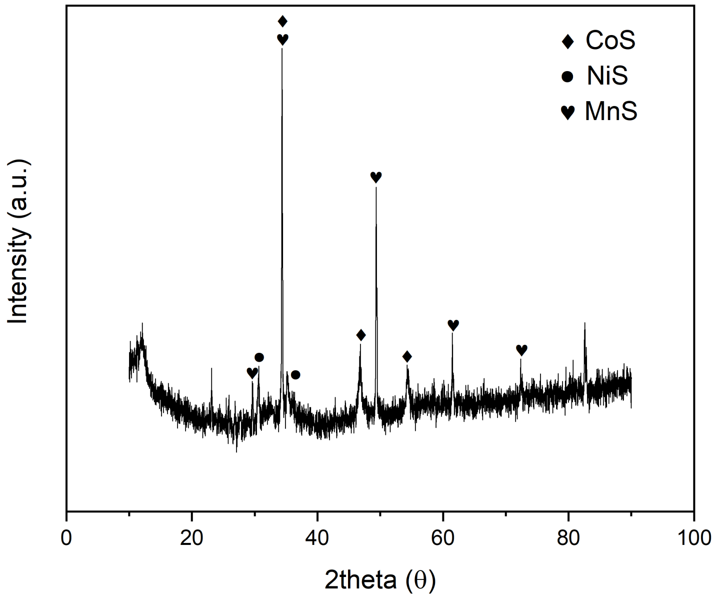

Fig. 8. XRD patterns of the residues obtained from the precipitation experiments. (Condition: initial concentrations of the Co(II), Ni(II), Mn(II) were fixed at 1000 mg/L, pH 2.0, a molar ratio of MnS/(Co(II)+Ni(II)) of 10, 400 rpm, room temperature)

3.5. Comparison between Na_2S/NaHS and MnS as a source of sulfide ion for the precipitation

In this work, MnS was employed as a source of sulfide ion, while Na_2S or NaHS is employed as a precipitant for the precipitation of metal sulfides. Traditional sulfide sources like Na_2S and NaHS offer some advantages as a precipitant including low cost, easy availability, and fast reaction rates. However, they often cause local super-saturation of sulfide ions, resulting in the formation of colloidal precipitates which makes filtration more difficult and in excessive reagent consumption. Moreover, introduction of sodium ions in the solution requires subsequent treatment step to recover pure metal compounds by separating sodium ions. Compared to Na_2S and NaHS, the solubility product of MnS is much smaller and control of solution pH is necessary to dissolve MnS. In homogeneous precipitation, the production rate of a precipitant would control the precipitation reaction, affecting the morphology of the precipitates and particle size distribution. Moreover, when MnS is employed as a sulfide ion source in the solution containing Mn(II), no other impure cations would be introduced to the filtrate, which has some advantages in terms of subsequent purification step. Although MnS is more expensive than Na_2S or NaHS, its stability and ability to minimize secondary sodium contamination could offer potential operational advantages. Nevertheless, a detailed techno-economic evaluation is still required to determine whether these benefits can offset the higher material cost. A comparison on the advantages and disadvantages between Na_2S/NaHS and MnS is listed in Table 2.

Long-term storage and usage conditions are crucial for industrial application. MnS as an inorganic solid is more stable than organic or soluble sulfide sources. Na_2S and NaHS are hygroscopic, prone to oxidation and can generate toxic H_2S gas upon exposure, requiring safety measures. By contrast, MnS is known for its chemical stability and has been used in industry, indicating that it can be stored and handled reliably over long periods.

Table 2. The comparison of advantages and disadvantages between Na_2S/NaHS and MnS as a precipitant (Zhang et al., 2023)

Sulfide source	Advantages	Disadvantages
Na_2S and NaHS	- Cheap - Fast reaction kinetics - Simple to use	- Low reaction efficiency and high consumption - Local supersaturation of sulfide ions - Formation of collodial precipitates difficult to filter - Introduction of sodium ions to the filtrate
MnS	- Possibility of accomplishing homogeneous precipitaion - Reduction of local super-saturation of sulfide ions in the solution - Improvement of particle size distribution - Avoid introducing other metal cations	- Higher price - Coating of the surface of MnS results in low reaction efficiency. - Control of solution pH

4. Conclusions

Hydrometallurgical treatments of end-of-life lithium-ion batteries generally result in the solutions containing Co(II), Mn(II) and Ni(II). To obtain high-purity precursor of Co(II) and Ni(II) for the manufacture of electrode materials for LIBs, separation of the above three metal ions is of importance. There is much difference in the precipitation pH among CoS, NiS and MnS. In this work, precipitation experiments were done to investigate the possibility of simultaneous separation of Co(II) and Ni(II) from Mn(II) by sulfide precipitation using MnS as a precipitant. Our results indicated that solution pH, dosage of MnS and reaction time greatly affected the precipitation of CoS and NiS. At least 30 mins of reaction time was necessary to dissolve the MnS in a solution with pH 2.0 at room temperature. When the concentrations of Co(II), Ni(II) and Mn(II) in the solution were 1000 mg/L, complete separation of Co(II) and Ni(II) by sulfide precipitation was obtained from the solution with pH 2.0 at a MnS/(Co(II)+Ni(II)) molar ratio of 10 and room temperature for 30 mins. When the initial concentration of Mn(II) and MnS dosage were fixed, the precipitation percentage of CoS and NiS was proportional to the concentration ratio Co(II) to Mn(II). When the concentration of Co(II)/Ni(II) and MnS dosage were fixed, the precipitation percentage of Co(II) and Ni(II) decreased as the initial concentration of Mn(II) decreased owing to encapsulation effect. XRD analysis of the precipitates verified the formation of CoS and NiS with high crystallinity, while the presence of MnS peaks highlighted incomplete dissolution under the conditions. This process offers several advantages, including control over sulfide ion release and high selectivity in metal recovery, compared to the processes employing traditional sulfide sources.

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