

Comparison of separation of Mn(II), Co(II), and Ni(II) by oxidative precipitation between chloride and sulfate solutions

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Abstract: In hydrometallurgy, precipitation would be easier and simpler than solvent extraction as a separation operation. In this work, the separation performance of Co(II), Mn(II) and Ni(II) by oxidative precipitation was investigated. For this purpose, NaClO was employed as an oxidizing agent and the separation behavior of the three ions was compared between chloride and sulfate solutions by varying some factors such as the dosage of NaClO, solution pH and reaction temperature. By controlling the molar ratio of NaClO to Mn(II), Mn(II) were easily separated as MnO₂ by oxidative precipitation from both chloride and sulfate solutions. At the same experimental conditions, precipitation percentage of Co(II) from chloride solution was higher than that from sulfate solution, which can be ascribed to the stronger tendency of Co(II) to form complexes with chloride ion than with sulfate ions. Addition of NaCl to sulfate solution and oxidative precipitation at high temperature enhanced the precipitation percentage of Co₂O₃ and thus separation degree between Co(II) and Ni(II) was improved. Under the optimum conditions, MnO₂ and Co₂O₃ powders with 99.9% purity were completely recovered by oxidative precipitation from chloride solution. By contrast, the purities of the MnO₂ and Co₂O₃ thus recovered from sulfate solution were only 76 and 91%, respectively. Our results indicated that chloride solution would be more effective than sulfate solution in separating Mn(II) and Co(II) by oxidative precipitation with NaClO. Therefore, the use of chloride-based leaching solutions such as HCl and FeCl₃ might be better for the leaching medium of spent lithium-ion batteries.

Keywords: oxidative precipitation, chloride ions, selectivity, recovery of strategic metals

1. Introduction

Spent lithium-ion batteries (LIBs) are considered to be important secondary resources due to their containing valuable metals such as lithium, cobalt, and nickel (Lei et al., 2022; Othman et al., 2020; Liu et al., 2019). The consumption of strategic metals for the manufacture of LIBs has grown annually and this trend is anticipated to continue due to the widespread application of LIBs in portable electronics since the end of the 20th century and the recent rapid growth of the electric vehicle market (Meshram et al., 2020; Al Sultan and Benli, 2023). Meanwhile, the buildup and improper disposal of enormous quantities of outdated LIBs endanger the environment and public health (Meshram et al., 2020; Kang et al., 2013). Thus, from an economic and environmental perspective, it is necessary to recover metals from spent LIBs, and several technologies for the recycling of spent LIBs have been developed (Jena et al., 2021; Rautela et al., 2023). Hydrometallurgical processes for the recycling of spent LIBs have been implemented on a considerable scale in the industry (Yao et al., 2018; Zhang et al., 1998; Joulié et al., 2014).

In the hydrometallurgy process, acidic leaching solutions such as sulfuric acid, hydrochloric acid, citric acid, oxalic acid, and methanesulfonic acid are commonly employed for the dissolution of metals from the powders of spent LIBs (Golmohammadzadeh et al., 2018; Ku et al., 2016; Tran et al., 2022; Nguyen and Lee, 2020; Lu et al., 2021). In general, H₂SO₄ and HCl are commonly employed in industry due to their benefits over other leaching agents in terms of the cost and metal dissolution effectiveness (Xu, et al., 2008; Li et al., 2022). After the leaching, their acidic leaching solutions typically contain Co(II),

Cu(II), Mn(II), and Ni(II). Among these ions, Cu(II) can be separated by cementation with base metal (Nguyen and Lee, 2023; Koseoglu et al., 2022; Tawonezvi et al., 2023). Then it is necessary to separate Co(II), Mn(II), and Ni(II) in order to recover pure compounds of these metals. Although lots of work have been reported on the separation of these three metal ions by solvent extraction due to its high efficiency and selectivity, precipitation is simpler and easier to operate industrially than solvent extraction and other separation methods such as ion exchange and reduction (Pohl, 2020). The advantages of chemical precipitation are process economics due to use of cheap reagent, extensive application range and the possibility of easy scale-up, while its drawbacks are the presence of a limit in the precipitation degree and in the selectivity. Some studies reported the possibility of separating Mn(II) and Co(II) from acidic solutions containing Ni(II) by oxidative precipitation (Nguyen and Lee, 2023; Joulié et al., 2014; Orue et al., 2021; Zhang et al., 2002). Among them, several kinds of oxidizing agents such as O_3 , NaClO, and gas mixture of SO_2 and O_2 were employed to separate Mn(II) and Co(II) in the form of MnO_2 and Co_2O_3 by controlling the molar ratio of oxidizing agent to Mn(II). However, it is not easy to separate Co(II) from Ni(II) by oxidative precipitation owing to co-precipitation of Ni(II) and incomplete precipitation of Co(II). Therefore, it is necessary to find a suitable oxidizing agents and some conditions by which the oxidative precipitation of Co(II) could be enhanced, resulting in complete separation of Co(II) and Ni(II).

The selection of oxidizing agent is critical when utilizing oxidative precipitation to separate target metal ions. Common oxidizing agents include hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), sodium hypochlorite (NaClO), and ozone (O_3), which can be employed in oxidative precipitation to separate metal ions (Singer and Reckhow, 1999). Considering the cost, appropriate reaction conditions, and reduction potential of oxidizing agents, NaClO is a better option for this study. In addition, the chemical properties of Co(II) and Ni(II) in aqueous solutions are very similar, which makes the separation of these two metal ions difficult. The Co(II) has a stronger tendency to form complexes with chloride ion than with sulfate ion. When a metal ion forms several complexes with a ligand, the mole fraction of the free metal ion would be drastically reduced, resulting a decrease in the reduction potential of the free metal ion. By utilizing this, the oxidative precipitation of Co(II) could be increased by introducing chloride ion into the solutions containing Co(II) and Ni(II).

In this work, separation behavior of Co(II), Mn(II) and Ni(II) by oxidative precipitation was compared between chloride and sulfate solution. In this work NaClO was employed as an oxidizing agent. Oxidative precipitation of Mn(II), Co(II) and Ni(II) from synthetic solutions of weak HCl and H_2SO_4 was investigated by varying some variables such as molar ratio of oxidizing agent to target metal ion, temperature, and solution pH. Especially the effect of adding NaCl or Na_2SO_4 to either HCl or H_2SO_4 solutions was investigated. Our results clearly indicated that Mn(II) and Co(II) can be easily separated from Ni(II) in HCl solution by oxidative precipitation. Namely, HCl solution is better than H_2SO_4 solution when employing oxidative precipitation to separate Mn(II), Co(II) and Ni(II) under the same experimental conditions, and addition of NaCl to weak acid solutions can enhance separation of Co(II) over Ni(II) by oxidative precipitation. Chloride-based leaching solutions are more favorable for the treatment of some resources containing Mn, Co, and Ni in terms of separation performance by oxidative precipitation.

2. Materials and methods

2.1. Reagents and chemicals

The powders obtained from the smelting reduction of spent LIBs at high temperature were dissolved in both kinds of acidic solutions and the leaching solutions contain Fe(III), Cu(II), Co(II), Mn(II), and Ni(II). Then, Fe(III) and Cu(II) were removed by hydrometallurgical methods like cementation and solvent extraction and the concentrations of the metal ions after the separation of Fe(III) and Cu(II) from the two acidic solutions were the same as shown in Table 1 (Wen and Lee, 2022). Synthetic solutions containing Co(II), Ni(II), and Mn(II) were prepared by dissolving their corresponding chloride and sulfate salts such as $CoCl_2 \cdot 6H_2O$ (Junsei Chemical Co., >97%, Japan), $MnCl_2 \cdot 4H_2O$ (Daejung Chemical & Metals Co., >98%, Korea), $NiCl_2 \cdot 6H_2O$ (Yakuri Pure Chemicals Co., >96%, Japan), $CoSO_4 \cdot 7H_2O$ (Daejung Chemical & Metals Co., >99.0%, Korea), $MnSO_4 \cdot nH_2O$ (Duksan Pure Chemicals Co., LTD, >99%, Korea), and $NiSO_4 \cdot 6H_2O$ (Daejung Chemical & Metals Co., >99%, Korea) in doubly distilled

water. Solution pH was adjusted by adding sulfuric acid (H₂SO₄, Daejung Chemical & Metals Co., >95%, Korea) or hydrochloric acid solution (HCl, Daejung Chemical & Metals Co., 35%, Korea). Other chemicals such as sodium chloride (NaCl, Shiwa Chemical Co., LTD, >99%, Japan), sodium sulfate (Na₂SO₄, Daejung Chemical & Metals Co., >99%, Korea), sodium hypochlorite (NaClO, Junsei Chemical Co. Ltd., >8%, Japan), sodium hydroxide (NaOH, Daejung Chemical & Metals Co., >97.0 %, Korea), and sodium oxalate (Na₂C₂O₄, Oriental Chemical Industries, >99%, Japan) were employed without any purification.

Table 1. The concentrations of Co(II), Mn(II) and Ni(II) in both synthetic HCl and H₂SO₄ solutions employed in the experiments

Acidic solutions	Metal ions, mg/L		
	Ni(II)	Co(II)	Mn(II)
HCl/H ₂ SO ₄	7756	1704	193

2.2. Procedure and analytical methods

All the oxidation and precipitation experiments in this work were carried out by slowly adding a specific amount of oxidative or precipitating agents to the determined volume (20 mL) of synthetic solutions in a 100-mL glass beaker with a cover to prevent the evaporation loss during the reaction. The stirring speed, reaction temperature, and time were controlled by a magnetic stirrer (Daihan Scientific Co., Korea). The resulting solutions after the experiments were filtered using filter paper (ADVANTEC No. 2, 110 mm, Toyo Roshi Kaisha, Ltd). The concentrations of the metal ions in the filtrate were measured by Inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany), and the pH of the solutions was determined using a pH meter (Orion Star thermo scientific pH meter, model A221, USA).

The oxidation or precipitation percentages of a metal ion were calculated as

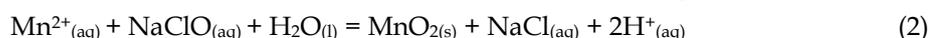
$$\text{Oxidation/Precipitation percentage (\%)} = \frac{m_{\text{initial}} - m_{\text{filtrate}}}{m_{\text{initial}}} \times 100 \quad (1)$$

where m_{initial} and m_{filtrate} are the mass of a metal ion before and after the oxidative or precipitating reactions, respectively.

3. Results and discussion

3.1. Separation of Mn(II) over Co(II) and Ni(II) from synthetic solutions of HCl and H₂SO₄ by oxidative precipitation

The oxidative precipitation reaction of Mn(II) by NaClO can be represented as (Nguyen and Lee, 2023)



Even in weak acidic solutions, the nature of a ligand affects the structure of the complex between the metal ion and the ligand, which might affect the chemical activity of the complexes. Therefore, the oxidative precipitation of Mn(II) by NaClO from H₂SO₄ and HCl solutions containing Co(II) and Ni(II) was investigated. In the treatment of the metallic alloys obtained by smelting reduction of spent lithium ion batteries at high temperature, the concentrations of Ni(II), Co(II), and Mn(II) in the filtrate after the separation of Cu(II) and Fe(III) were 7756, 1704, and 193 mg/L, respectively and solution pH was 3.0. Therefore, the concentrations of Ni(II), Co(II), and Mn(II) in the synthetic H₂SO₄ and HCl solutions employed in this work were kept at 7756, 1704, and 193 mg/L. The molar ratio of NaClO to Mn(II) was varied from 1 to 5 in both acidic synthetic solutions and the initial pH of solutions was fixed at 3. The reactions were performed with 400 rpm of stirring speed at 25°C for 30 mins. Fig. 1 shows that the precipitation percentage of Mn(II) from the HCl solution remarkably increased to 100% as the molar ratio of NaClO to Mn(II) increased to 3. It was noticeable that the decrease in the concentration of Co(II) (approximately 4.7%) was observed when the molar ratio of NaClO to Mn(II) was higher than 4, owing to the oxidative precipitation of Co₂O₃, while the change in Ni(II) concentration was not observed. These results indicated that NaClO could be a potential agent for the selective separation of Co(II) over Ni(II)

by the oxidative precipitation from HCl solution. Meanwhile, the precipitation percentage of Mn(II) from the H₂SO₄ solution was lower than that from the HCl solution at the same conditions. Namely, the precipitation percentage of Mn(II) was increased from 50 to 90% as the molar ratio of NaClO to Mn(II) was increased from 3 to 5 (see Fig. 2). The selective precipitation of Mn(II) over Co(II) and Ni(II) by NaClO solution was ascribed to the difference in the redox potentials of the metal ions in acidic solutions (See Table 2). The Pourbaix diagram indicates that variations in pH can influence the oxidation state of metal ions, which in turn can affect the redox reactions (Cook and Olive, 2012). For example, Ni(II) may be oxidized to Ni₂O₃ when the pH value is around 3.

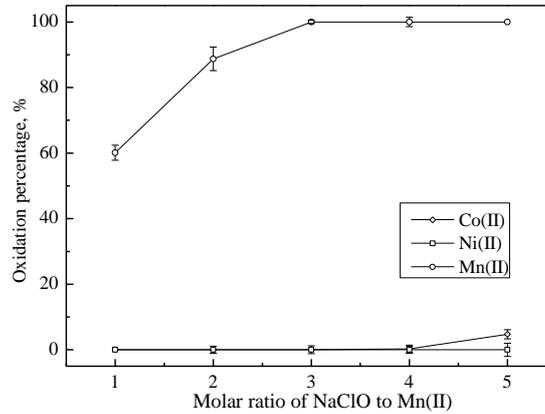


Fig. 1. Effect of the molar ratio of NaClO to Mn(II) on the oxidative precipitation of the metal ions from synthetic HCl solution. (pH 3, 30 min, 400 rpm, 25°C)

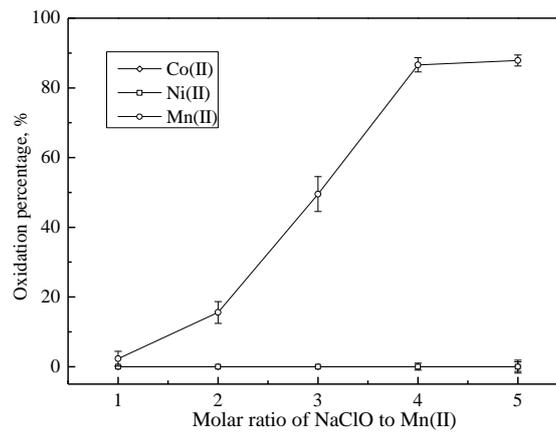


Fig. 2. Effect of the molar ratio of NaClO to Mn(II) on the oxidative precipitation of the metal ions from synthetic H₂SO₄ solution. (pH 3, 30 min, 400 rpm, 25°C)

Table 2. The reduction potential values of MnO₂, Co₂O₃, and Ni₂O₃ from acidic solution at 25°C

Half reactions	E ₀ , V
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e} = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{Co}_2\text{O}_3 + 6\text{H}^+ + 2\text{e} = 2\text{Co}^{2+} + 3\text{H}_2\text{O}$	1.746
$\text{Ni}_2\text{O}_3 + 6\text{H}^+ + 2\text{e} = 2\text{Ni}^{2+} + 3\text{H}_2\text{O}$	1.753
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e} = \text{Cl}^- + 2\text{OH}^-$	0.89

These results indicated that chloride ions have a positive effect on the precipitation of Mn(II) compared to sulfate ions. Although the precipitation percentage of Mn(II) from H₂SO₄ solution was lower than that from HCl solution, no precipitates of Co(II) and Ni(II) were formed from H₂SO₄ solution. Therefore, H₂SO₄ solution is more effective in separating Mn(II) by oxidative precipitation than HCl

solution on the basis of separation degree. Therefore, the effect of reaction temperature on the precipitation of Mn(II) from the H₂SO₄ solution was investigated. The reaction temperature was varied from 25 to 95°C by fixing the molar ratio of NaClO to Mn(II) at 4. In Fig. 3, the precipitation percentage of Mn(II) reached approximately 100% when the reaction temperature was 60 °C, while that of Co(II) and Ni(II) was negligible.

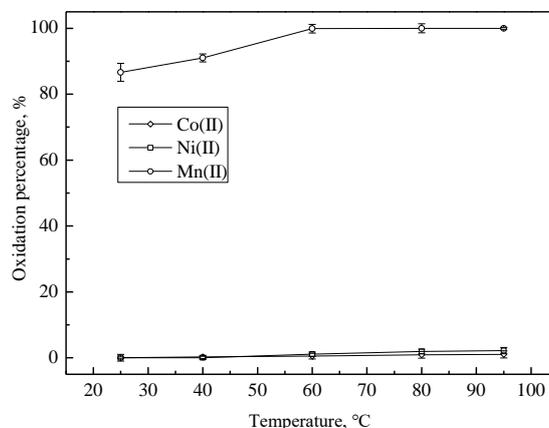


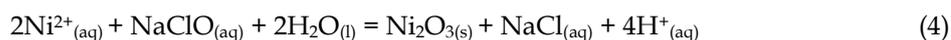
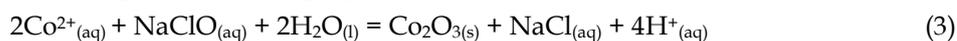
Fig. 3. Effect of temperature on the oxidative precipitation of the metal ions from synthetic H₂SO₄ solution. (A molar ratio of 4 for NaClO to Mn(II), pH 3, 30 min, 400 rpm)

Thus, the selective precipitation of Mn(II) over Co(II) and Ni(II) from two acidic solutions was achieved using NaClO as an oxidative precipitating agent. The best conditions for the precipitation of Mn(II) were determined to be at the molar ratio of 3 for NaClO to Mn(II), pH 3, 25°C, and 30 mins for the HCl solution and at the molar ratio of 4 for NaClO to Mn(II), pH 3, 60°C, 30 mins for the H₂SO₄ solution. Compared to HCl solution, the precipitation percentage of Mn(II) from H₂SO₄ solution was lower. Among the metal ions, Mn(II) can be completely oxidized at suitable conditions from HCl solution and the separation factor between Mn(II) and the sum of Co(II) and Ni(II) from H₂SO₄ solution was higher than 60000, indicating that the separation effect is also obvious from H₂SO₄ solution even though a certain amount of Co(II) and Ni(II) were co-oxidized with Mn(II).

3.2. Separation of Co(II) from HCl and H₂SO₄ filtrates containing Ni(II) after removal of Mn(II)

3.2.1. Effect of molar ratio of NaClO to Co(II) on the precipitation of Co(II) from HCl and H₂SO₄ solutions containing Ni(II)

The concentrations of Ni(II) and Co(II) in the filtrate after the separation of Mn(II) were determined to be 7701 and 1689 mg/L, respectively. The addition of NaClO solution during oxidative precipitation of Mn(II) caused a slight decrease in metal concentrations. Since the chemical properties of Co(II) and Ni(II) are rather similar, the complete separation of these two metals by precipitation might be difficult. The results in the previous section indicate that Co(II) could be selectively oxidized to Co₂O₃ over Ni(II) by NaClO from HCl solution (See Fig. 1). The oxidative precipitation reaction of Co(II) and Ni(II) with NaClO can be represented by Eqs. (3) and (4) (Speight, 2005).



To investigate the effect of the dosage of NaClO on the precipitation of Co(II) from H₂SO₄ and HCl solutions, the molar ratio of NaClO to Co(II) was varied from 4 to 12 and the initial pH, stirring speed, reaction temperature, and time were fixed at 3.0, 400 rpm, 25°C, and 30 mins, respectively. As represented in Figs. 4 and 5, the precipitation percentage of Co(II) from both HCl and H₂SO₄ filtrates significantly increased with the dosage of NaClO. In Fig. 4, the precipitation percentage of Co(II) in the HCl solution increased from 90% to 99% as the molar ratio of NaClO to Co(II) increased from 4 to 8 and no Ni(II) was precipitated. With the further increase of the molar ratio NaClO, there was no change in the precipitation percentage of Co(II), whereas 5% Ni(II) was precipitated. These results indicate that

selective separation of Co(II) from the HCl solution containing Ni(II) is possible when the molar ratio of NaClO to Co(II) was lower than 8.

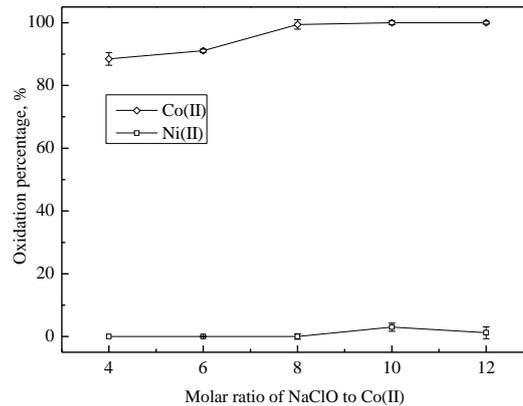


Fig. 4. Effect of the molar ratio of NaClO to Co(II) on oxidative precipitation of Co(II) and Ni(II) from synthetic HCl solution. (pH 3, 30 min, 400 rpm, 25°C)

The precipitation percentage of Co(II) by NaClO from H₂SO₄ solution was lower than that from HCl solution at the same experimental conditions (see Fig. 5). When the molar ratio of NaClO to Co(II) was 8, the precipitation percentages of Co(II) and Ni(II) from H₂SO₄ solution were 87% and 3%, respectively. These results agreed well with the reported data about the co-precipitation of Ni(II) and Co(II) when the molar ratio of NaClO was high (Nguyen and Lee, 20232). Therefore, a molar ratio of 6 for NaClO to Co(II) was selected for the oxidative precipitation of Co(II) from H₂SO₄ solution, at which conditions the precipitation percentages of Co(II) and Ni(II) were 84% and zero. To enhance the precipitation efficiency of Co(II) from the H₂SO₄ solution and improve its purity, the effect of several factors such as pH, the presence of chloride and sulfate anions, and temperature was investigated, which can significantly affect the redox potential of NaClO and the formation of metal complexes.

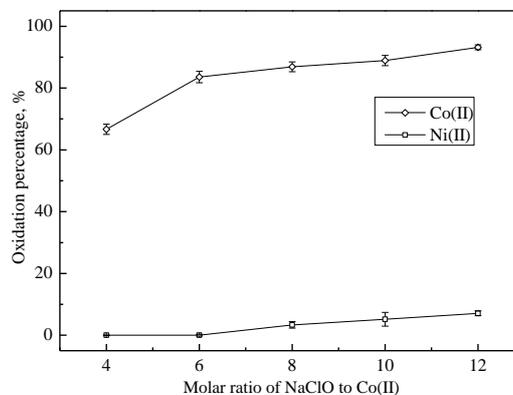


Fig. 5. Effect of the molar ratio of NaClO to Co(II) on the oxidative precipitation of Co(II) and Ni(II) from synthetic H₂SO₄ solution. (pH 3, 30 min, 400 rpm, 25°C)

3.2.2. Effect of several factors on the precipitation of Co(II) from HCl and H₂SO₄ solutions containing Ni(II)

Oxidative precipitation reactions of Co(II) and Ni(II) with NaClO, Eqs. (3) and (4) show that hydrogen ions would be produced during the reaction and thus higher pH would enhance the precipitation of both ions. The basicity of ClO⁻ ion is 3.31×10^{-7} and thus solution pH would affect the effective concentration of ClO⁻ which can take part in the oxidative precipitation of Co(II) and Ni(II). To consider the effect of solution pH on the selective precipitation of Co(II), the pH of the H₂SO₄ solution was varied from 2 to 5. In these experiments, the molar ratio of NaClO to Co(II), stirring speed, reaction temperature, and time were fixed at 6, 400 rpm, 25°C, and 30 min, respectively. Fig. 6 indicates that the precipitation percentages of Co(II) and Ni(II) were constant at 84% and zero in these pH ranges. These

results could be attributed to the insignificant changes in the chemical activity of NaClO and the speciation of the predominant species of both ions in the studied pH ranges. Therefore, pH solution of 3 was selected in further experiments and the effect of adding chloride and sulfate anions on the precipitation of Co(II) was studied.

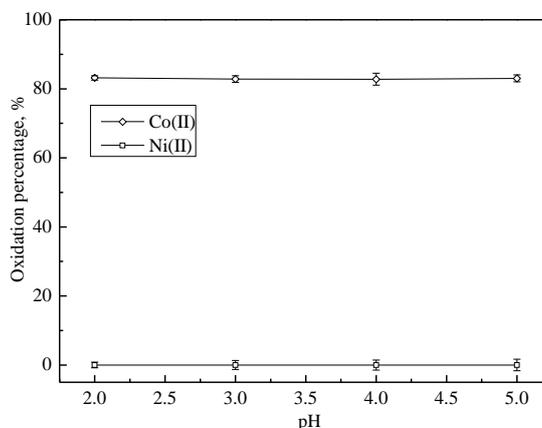


Fig. 6. Effect of initial pH on the oxidative precipitation of Co(II) and Ni(II) from synthetic H_2SO_4 solution. (A molar ratio of 6 for NaClO to Co(II), 30 min, 400 rpm, 25°C)

Some works have reported that addition of chloride or sulfate ion to H_2SO_4 solution would affect the oxidative precipitation of Co(II) and Ni(II) (Lin et al., 1998). In order to investigate these effects, varying amounts of NaCl and Na_2SO_4 were added to the H_2SO_4 solution containing Co(II) and Ni(II). Experiments were performed by fixing the molar ratio of NaClO to Co(II) at 6 under the following conditions: 400 rpm, initial solution pH 3, 30 mins, and 25°C. Fig. 7a shows that the precipitation percentage of Co(II) significantly rose from 84 to 98% as NaCl concentration increased from 0 to 50 g/L and was constant with the further increase of NaCl concentration to 100 g/L. In these experimental ranges, the precipitation percentage of Ni(II) was below 2%. When the concentration of Na_2SO_4 in the solution was changed from zero to 50 g/L, there was no change in the precipitation percentages of both Co(II) and Ni(II) and addition of Na_2SO_4 did not affect the precipitation of both ions (see Fig. 7b). The enhancement in the oxidative precipitation of Co(II) in presence of chloride ion might be ascribed to the stronger tendency of Co(II) to form complexes with chloride ion compared to Ni(II). In these circumstances, the mole fraction of free Co(II) would be rapidly decreased with the concentration of chloride ion, resulting in an increase in the oxidation potential of Co(II). By Contrast, the complex formation constant of Ni(II) with chloride ion is small and the effect of adding chloride ion was not pronounced for the oxidative precipitation of Ni(II), while sulfate complexes with Co(II) and Ni(II) are insignificant. The complex formation constants of Co(II) and Ni(II) with chloride and sulfate ion are listed in Table 3. The difference in the oxidative precipitation behavior of Co(II) in chloride and sulfate solutions could be related to the formation of stable complexes of Co(II) with chloride ions such as $CoCl^+$, $CoCl_2$, $CoCl_3^-$, and $CoCl_4^{2-}$, which might enhance the oxidation of Co(II) to Co(III) (Lee and Oh, 2005). Table 3 shows that Co(II) has a stronger tendency to form complexes with chloride ions compared to Ni(II), and the formation of these complexes significantly reduces the concentration of free metal ion in the solution. In this case, the reduction potential of the free Co(II) ion would be significantly decreased, which can make the oxidation of the corresponding metal ion occur easily.

Our results show that separation of Co(II) by oxidative precipitation from Ni(II) in H_2SO_4 solution was possible but the precipitation percentage of Co(II) was about 84%. When NaCl was added to H_2SO_4 solution, the oxidative precipitation percentage of Co(II) was significantly improved. Therefore, further experiments were done by adding 50 g/L of NaCl to H_2SO_4 solution. In addition, further experiments were done by adding various amounts of NaCl and Na_2SO_4 to the HCl solution. In these experiments, the molar ratio of NaClO to Co(II) was fixed at 6. Fig. 8 shows that it was possible to completely separate Co(II) from Ni(II) in synthetic HCl solution when NaCl concentration was controlled to 6 g/L by fixing the molar ratio of NaClO to Co(II) at 8. However, the oxidation of Co(II) was not significantly affected by the addition of Na_2SO_4 . Moreover, this figure shows that the addition of NaCl to HCl solution

increased the oxidation of Co(II) via a change in cobalt speciation rather than a change in ionic strength. Our results clearly showed that addition of chloride ion to either H₂SO₄ or HCl solution showed a positive effect on the separation of Co(II) from Ni(II) by oxidative precipitation with NaClO.

The effect of reaction temperature on the precipitation of Co(II) with the addition of NaCl was considered. Reactions was carried out from 25 to 95°C by fixing the molar ratio of NaClO to Co(II) at 6 under the following conditions: initial pH 3, 30 mins reaction time, 400 rpm stirring speed, and 50 g/L of NaCl addition. Fig. 9 shows that the precipitation percentage of Co(II) gradually increased as the reaction temperature increased and reached 99.6% at 95°C, while 2% of Ni(II) was co-precipitated at 95°C.

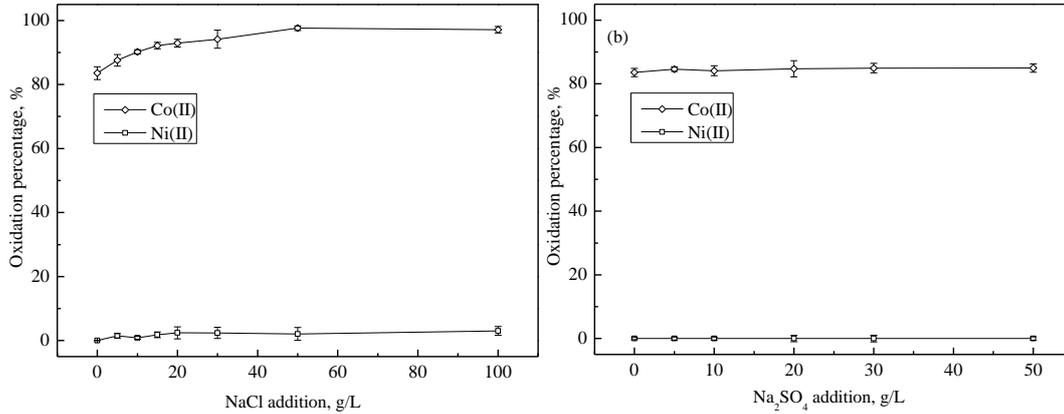


Fig. 7. Effect of addition of NaCl and Na₂SO₄ on the oxidative precipitation of Co(II) and Ni(II) from synthetic H₂SO₄ solution (A molar ratio of 6 for NaClO to Co(II), pH 3, 30 min, 400 rpm, 25°C)

Table 3. The complex formation constants of Co(II) and Ni(II) with chloride and sulfate ions at 25°C

Reaction	LogK
$\text{Co}^{2+} + \text{Cl}^- = \text{CoCl}^+$	0.22
$\text{Co}^{2+} + 2\text{Cl}^- = \text{CoCl}_2$	-3.95
$\text{Co}^{2+} + 3\text{Cl}^- = \text{CoCl}_3^-$	-3.02
$\text{Co}^{2+} + 4\text{Cl}^- = \text{CoCl}_4^{2-}$	-9.06
$\text{Ni}^{2+} + \text{Cl}^- = \text{NiCl}^+$	-1.29
$\text{Ni}^{2+} + 2\text{Cl}^- = \text{NiCl}_2$	-0.93
$\text{Ni}^{2+} + 3\text{Cl}^- = \text{NiCl}_3^-$	-2.48

Ref: (Diebler, 1983; Liu et al., 2012)

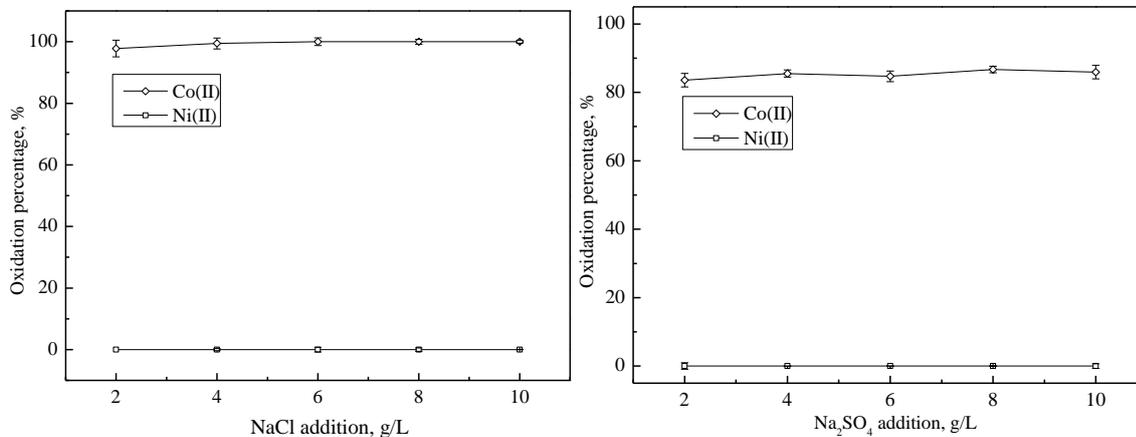


Fig. 8. Effect of addition of NaCl and Na₂SO₄ on the oxidative precipitation of Co(II) and Ni(II) from synthetic HCl solution. (A molar ratio of 8 for NaClO to Co(II), pH 3, 30 min, 400 rpm, 25°C)

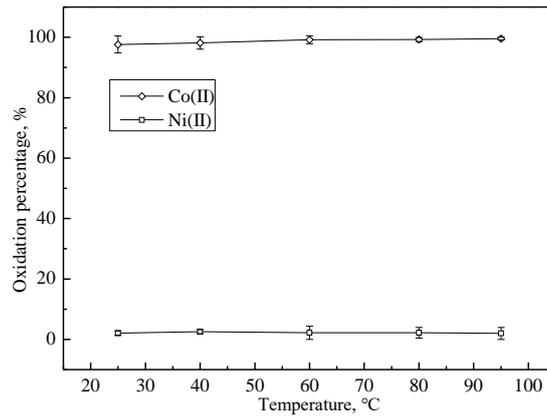


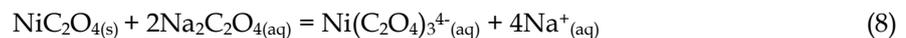
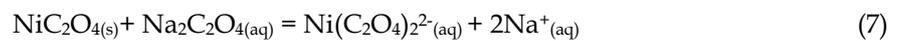
Fig. 9. Effect of the temperature on the oxidative precipitation of Co(II) and Ni(II) from synthetic H₂SO₄ solution. (A molar ratio of 6 for NaClO to Co(II), pH 3, 50 g/L of NaCl addition, 30 min, 400 rpm)

Our results showed that the precipitation percentage of Co(II) and Ni(II) in the H₂SO₄ solution is lower than that from the HCl solution. However, the precipitation efficiency of Co(II) in the H₂SO₄ solution can be improved by adding NaCl and by increasing temperature. As a result, Co(II) can be completely oxidized over Ni(II) in HCl solution and the separation factor of Co(II) to Ni(II) in H₂SO₄ is approximately 10895. Compared to the separation factor for the oxidation of Mn(II) over Co(II) and Ni(II), selective oxidation of Co(II) from Ni(II) is relatively difficult due to the similar chemical properties of Co(II) and Ni(II) in solution. The best conditions for the oxidative precipitation of Co(II) over Ni(II) from acid solutions were as follows:

- (1) HCl solution: pH 3, 400 rpm, 25°C, 30 min, a molar ratio of 8 for NaClO to Co(II), 6 g/L of NaCl addition
- (2) H₂SO₄ solution: pH 3, 400 rpm, 95°C, 30 min, a molar ratio of 6 for NaClO to Co(II), 50 g/L of NaCl addition

3.3. Precipitation of Ni(II) from the H₂SO₄ and HCl filtrates after the separation of Mn(II) and Co(II)

After the separation of Mn(II) and Co(II) by oxidative precipitation from HCl and H₂SO₄ solutions, the concentration of Ni(II) in filtrates was approximately 7212 mg/L. The solubility product values of Ni(OH)₂ and NiC₂O₄ at 25°C are 5.48×10^{-16} and 4.00×10^{-10} , respectively (Speight, 2005). Therefore, these Ni(II) compounds can be recovered from the respective filtrates of HCl and H₂SO₄ solutions. The following reactions represent the precipitation of Ni(II) hydroxide and oxalate and the subsequent re-dissolution of the Ni(II) oxalates when the amount of sodium oxalate is in excess. Therefore, it is important to find the optimum concentration of sodium oxalate to get the maximum recovery of Ni(II) oxalate.



First, in order to precipitate Ni(OH)₂, the pH of the filtrates was adjusted from 7 to 11 using NaOH solution and the experiments were done at 25°C for 30 mins. According to Fig. 10, there was an insignificant difference in the precipitation percentage of Ni(II) between HCl and H₂SO₄ solutions and most of Ni(II) was precipitated at pH 11. Therefore, pH 11 was the optimum condition for the precipitation of Ni(OH)₂.

Second, the precipitation experiments of NiC₂O₄ from the HCl and H₂SO₄ solutions were done by varying the molar ratio of Na₂C₂O₄ to Ni(II) from 0.8 to 1.2. The initial pH of the solutions was kept at 3 and reactions were carried out at 25°C for 60 mins with a stirring speed of 400 rpm. Fig. 11 clearly shows that there was an optimum molar ratio of Na₂C₂O₄ at which the precipitation percentages of Ni(II) in both acid solutions were maximum. The maximum precipitation percentages of Ni(II) were 98.2% for

HCl and 94.2% for H_2SO_4 solution when the molar ratios of $\text{Na}_2\text{C}_2\text{O}_4$ to Ni(II) were 1.0 and 0.9, respectively. The decrease in the precipitation percentage of NiC_2O_4 when the molar ratios of $\text{Na}_2\text{C}_2\text{O}_4$ to Ni(II) were higher than those values is related to the formation of soluble Ni(II) complexes like $\text{Ni}(\text{C}_2\text{O}_4)_2^{2-}$ ($K = 10^{3.05}$) and $\text{Ni}(\text{C}_2\text{O}_4)_3^{4-}$ ($K=10^{1.36}$) as represented in Eqs. (7) and (8) (Watters and DeWitt, 1960). These results indicated that it is difficult to completely precipitate NiC_2O_4 at 25°C for 60 mins. Therefore, it might be said that precipitation of $\text{Ni}(\text{OH})_2$ is better than that of NiC_2O_4 on the basis of Ni(II) recovery from the filtrates.

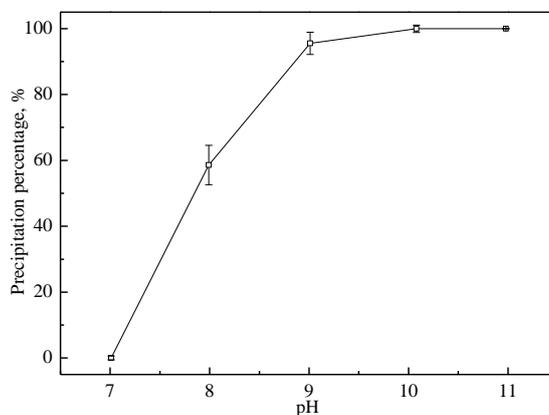


Fig. 10. Effect of solution pH on the precipitation of Ni(II) hydroxides by adding NaOH solution to the filtrate containing Ni(II). (30 min, 400 rpm, 25°C)

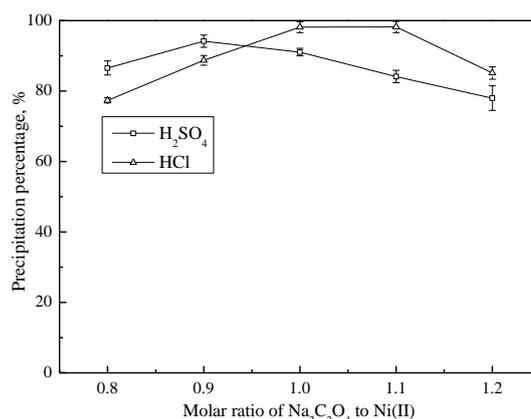


Fig. 11. Effect of the molar ratio of $\text{Na}_2\text{C}_2\text{O}_4$ to Ni(II) on the precipitation of Ni(II) oxalates from synthetic HCl and H_2SO_4 solution (pH 3, 60 min, 400 rpm, 25°C)

3.4. Comparison of the separation of Co(II), Ni(II), and Mn(II) between HCl and H_2SO_4 solutions by oxidative precipitation

In this work, oxidative precipitation experiments were carried out to investigate the separation of Mn(II), Co(II), and Ni(II) from synthetic acidic solutions of H_2SO_4 and HCl. NaClO was employed as an oxidizing agent and Mn(II) and Co(II) were sequentially separated by precipitation of MnO_2 and Co_2O_3 , leaving Ni(II) in the filtrate. Our results indicated that there is a certain difference in the oxidative precipitation behavior of the three metal ions between HCl and H_2SO_4 solutions. In comparing the separation efficiency of the metal ions by oxidative precipitation, it is also important to consider the recovery and the purity of the precipitates thus obtained. The purity of the precipitates depends on the sensitivity of the oxidative precipitation reaction to the molar ratio of NaClO to metal ions. Table 4 lists the optimum conditions for the selective precipitation of Mn(II) and Co(II) and compares the recovery and purity of the precipitates obtained at the corresponding conditions from HCl and H_2SO_4 solutions. The recovery percentage and purity of MnO_2 and Co_2O_3 from HCl solution were higher than 99%. By contrast, the purity of the oxides of Mn(II) and Co(II) obtained from H_2SO_4 solution was only 77 and 91%, respectively. Therefore, it can be said that HCl solution is better than H_2SO_4 solution in separation

of Mn(II) and Co(II) by oxidative precipitation. In general, Mn(II) and Co(II) have a stronger tendency to form complexes with chloride ions than with sulfate ions. Formation of complexes reduces the concentration of the free metal ions, resulting a decrease in the reduction potential of the metal ions. Therefore, our results show that the oxidative precipitation percentages of Mn(II) and Co(II) from HCl solution was higher than those from H₂SO₄ solution. In addition, addition of NaCl to H₂SO₄ solution at higher temperature shows a favorable effect on the oxidative precipitation of Co(II).

Table 4. A comparison of the conditions and performance for the oxidative precipitation of Mn(II) and Co(II) between HCl and H₂SO₄ solutions

Acid solutions	Mn(II) oxidation		Co(II) oxidation	
	Conditions	Recovery and Purity, %	Conditions	Recovery and Purity, %
H ₂ SO ₄	pH=3, 60°C, molar ratio of NaClO to Mn(II)=4	Recovery = 99.9%; Purity = 76.7%	pH=3, 95°C, molar ratio of 6 for NaClO to Co(II), NaCl: 50 g/L	Recovery = 96.5%; Purity = 91.1%
	pH=3, 25°C, molar ratio of NaClO to Mn(II)=3	Recovery = 99.9%; Purity = 99.9%	pH=3, 25°C, molar ratio of 8 for NaClO to Co(II)	Recovery = 99.9%; Purity = 99.9%

In hydrometallurgy, solvent extraction is generally employed for the separation of Mn(II), Co(II) and Ni(II) from the leaching solutions of diverse resources. However, our results clearly indicated that oxidative precipitation by NaClO is a simple operation by which Mn(II) and Co(II) can be sequentially separated from the solutions containing Ni(II) at room temperature by careful control of the molar ratio of NaClO. In this study, the oxidation reaction kinetics is substantially faster than precipitation kinetics, and our data showed that an increase in reaction temperature significantly accelerated the overall reaction kinetics. Furthermore, the oxidation-reduction potential (ORP) values before and after the oxidative precipitation reactions were measured. The ORP values of the solutions before experiments were in the range from 57 to 92 mV. When some amount of NaClO was introduced to the solutions under the optimal conditions, the ORP values of the solutions were rapidly increased to around 1035 to 1165 mV. According to the Pourbaix diagrams, MnO₂ and Co₂O₃ are stable at these potentials when solution pH is 3 (Cook and Olive, 2012). In addition, compared to other oxidants such as H₂O₂, NaClO₃, and KMnO₄, the price of NaClO is relatively cheap. Although the cost for the production of ozone is relatively cheap, NaClO is better than ozone on the light of storage and exhaust gas treatment. Considering that spent LIBs contain these three metal oxides and HCl solution is more effective in separating Mn(II) and Co(II) by oxidative precipitation, chloride based leaching solutions like HCl and FeCl₃ solution can be employed as a leaching agent for the treatment of spent LIBs.

4. Conclusions

The main components of spent lithium-ion batteries are cobalt, manganese and nickel oxides. Therefore, the separation of these three metal ions from the leaching solutions of spent LIBs is of importance in the recovery of these metal compounds with high purity. The oxidative precipitation behavior of Mn(II), Co(II), and Ni(II) by using NaClO as an oxidizing agent was compared between weak HCl and H₂SO₄ solutions. Mn(II) was selectively precipitated over Co(II) and Ni(II) by oxidative precipitation with NaClO from both weak HCl and H₂SO₄ solutions. Although complete recovery of Mn(II) in the form of MnO₂ was possible from both solutions, HCl solution was found to be better than H₂SO₄ solution in terms of the purity of the MnO₂ thus obtained. MnO₂ powders with 99.9% purity were recovered from HCl solution at the following conditions: a molar ratio of 3 for NaClO to Mn(II), pH 3, and 25°C. By contrast, the purity of MnO₂ powders recovered from H₂SO₄ solution was only 77%. In separating Co(II) and Ni(II) from HCl and H₂SO₄ solutions after removal of Mn(II), Co(II) was selectively precipitated over Ni(II) by NaClO. The purities of the Co₂O₃ powders from HCl and H₂SO₄ solutions were 99.9 and 91%, respectively, indicating that HCl solution was better in separating Co(II) by oxidative precipitation

than H₂SO₄ solution. At the same experimental conditions, the precipitation percentages of MnO₂ and Co₂O₃ from HCl solution was higher than those from H₂SO₄ solution. Addition of NaCl to either HCl or H₂SO₄ solution enhanced the oxidative precipitation of Co(II) over Ni(II). Ni(II) in the final filtrate after separation of Mn(II) and Co(II) can be recovered as Ni(II) hydroxides by adjusting solution pH at 11. In terms of the recovery percentage and the purity of the powders recovered by oxidative precipitation, HCl solution is more effective than H₂SO₄ solution as a medium. Therefore, use of chloride based leaching solutions for the dissolution of some resources containing these three components is favorable on the light of the separation efficiency by oxidative precipitation.

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