

Selective nickel precipitation efficiency from cobalt in citrate media with DMG after lithium solvent extraction

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A novel lithium-ion battery (LIB) recycling process utilising citric acid as lixiviant has been developed, which enables the separation of lithium under weak acidic conditions, producing a raffinate rich in cobalt and nickel. This paper investigates the separation of nickel from the raffinate, produced through the novel recycling processes, with a precipitation process. Dimethylglyoxime (DMG) was selected as precipitant due to its high selectivity for nickel, which has shown promise for nickel separation in different processes. The influence of the Ni/DMG stoichiometric ratio was investigated and it was concluded a Ni/DMG ratio of at least 0.2 is required for near complete nickel precipitation. The Ni/DMG ratio also played a crucial role in the co-precipitation of cobalt and residual lithium and manganese, as their co-precipitation increased gradually as the Ni/DMG ratio decreased from 0.3 to 0.1. The impact of pH on the precipitation of nickel was negligible between a pH of 6 and 8, however, the co-precipitation of cobalt and residual manganese was observed to increase notably as the pH decreased from 7 to 6. The optimum nickel precipitation was therefore determined to be with a Ni/DMG ratio of 0.2 at a pH of 8, where 98.5% nickel could be precipitated with roughly 20% cobalt co-precipitation. The low solubility of DMG in water remains a concern as the addition of the precipitant leads to the dilution of cobalt in the filtrate, which must be recovered in a subsequent process, and therefore the maximum concentration DMG precipitant should be used.

Keywords: Hydrometallurgy, lithium-ion batteries, citric acid, precipitation, nickel separation

INTRODUCTION

The recycling of lithium-ion batteries (LIBs) has received continued interest in recent years due to the increased adoption of LIBs in consumer electronics, electric vehicles, and stationary energy storage systems. The LIBs from these widespread technologies will produce up to 464,000 tonnes of discarded LIBs annually in China alone by 2025 (Zhao *et al.*, 2019), after which their disposal poses significant concerns due their hazardous and toxic components (Kang *et al.*, 2013). Recycling scrap LIBs not only reduces the impact of their toxic and hazardous components (Wang *et al.*, 2014), but also provides significant economic benefits due to the variety of metals they contain like cobalt, lithium, nickel, manganese, copper, and aluminium (Ali *et al.*, 2021).

Research on LIB recycling has focussed on hydrometallurgical processes in recent years due to their high metal extraction, high metal purity, low energy consumption, and reduced gas emissions (Lie and Liu, 2021). Conventional hydrometallurgical LIB recycling processes use strong inorganic acids like H₂SO₄ (He *et al.*, 2017), however, these processes produce dangerous gasses like SO₃ which are undesired (Li *et al.*, 2010). New research has investigated the potential of more environmentally friendly and sustainable lixivants like citric acid, which is less toxic, does not produce toxic gasses, is cost effective, and has shown good leaching performance (Golmohammadzadeh *et al.*, 2018; Meng *et al.*, 2020). One of the major impediments to the adoption of citric acid for LIB recycling includes the complicated metal separation caused by the chelating properties of citric acid.

A study by Punt *et al.*, (2021) developed a novel recycling process which prioritises the separation of lithium under weak acidic conditions through solvent extraction prior to nickel and cobalt recovery. The study by Punt *et al.*, (2021), however, does not separate the nickel and cobalt remaining in the raffinate from the lithium solvent extraction. No solvent extraction process has been identified for the separation of cobalt and nickel from citrate media, and therefore the separation of nickel and cobalt by precipitation was considered for this study.

Both cobalt and nickel are transition metals that can be precipitated under alkaline conditions to form their respective hydroxides, namely, $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$. Joo *et al.*, (2016) illustrated that the separation of cobalt and nickel through hydroxide precipitation is however not possible due to their similar properties, which leads to their metal hydroxide precipitates forming at similar pH levels. Zou *et al.*, (2013) utilised the similar properties of cobalt, nickel, and manganese to precipitate all three metals together as a mixed metal product. The drawbacks of a mixed metal product include the adjustment required to achieve the desired stoichiometric ratio and the fact that only cathode chemistries similar to those of the recycled LIBs can be produced. Producing individual metal product streams during LIB recycling will enable the production of new cathodic materials (Yoshino, 2014) developed with advances in material science to improve the performance of LIBs (Wang *et al.*, 2014).

The high selectivity of dimethylglyoxime (DMG) for nickel as analytical reagent has been well published (Diehl, 1940) with studies investigating the separation of nickel from HCl, H_2SO_4 , and citric acid media (Chen and Zhou, 2014; Wang *et al.*, 2009; Yang *et al.*, 2021). Wang *et al.*, (2009) determined that after the separation of manganese by precipitation with KMnO_4 , the nickel could be selectively precipitated, after the addition of a NH_3 solution to form $[\text{Ni}(\text{NH}_3)_6]^{2+}$, from cobalt in a 4M HCl lixiviant.

Chen and Zhou (2014) used the same DMG precipitation technique to separate nickel from a 2M citric acid LIB pregnant leach solution (PLS). The study added a 0.05M DMG reagent to the citrate leach solution at 25°C to selectively precipitate the nickel from the cobalt and lithium. The study determined that a maximum of 98% nickel precipitation could be achieved at a pH of 8 and Ni/DMG ratio of 0.5. It was further illustrated that the nickel can then be recovered from the precipitate by dissolving the Ni-DMG precipitate in 4M HCl to recover NiCl_2 to solution and the DMG as a white powder, which can then be reused in a cyclical fashion. The regeneration of DMG through wet chemical methods are of vital importance as DMG cannot be recovered through calcination, which has been one of the major hinderances in the adoption of DMG as precipitant for industrial applications (Rath *et al.*, 2018).

The separation of nickel from cobalt in citrate media is therefore theorised to be good with DMG, with previous studies like that of Chen and Zhou (2014) illustrating the separation performance of nickel when separated first. Nickel is however strongly bound to the citrate ligands in the lixiviant and forms stable complexes with citric acid (Hedwig *et al.*, 1980; Zelenin, 2007). The separation of nickel from cobalt may therefore be impaired after the extraction of other metals in prior separation processes (Punt *et al.*, 2021), as the molar ratio of citrate to nickel increases when the other metals are separated. This study will investigate the nickel separation performance from cobalt in citrate media using DMG, after the removal of aluminium, manganese, and lithium as illustrated in Figure 1. The effective separation of nickel from cobalt will produce individual metal product streams from scrap LIBs using a novel citrate-based hydrometallurgical recycling process.

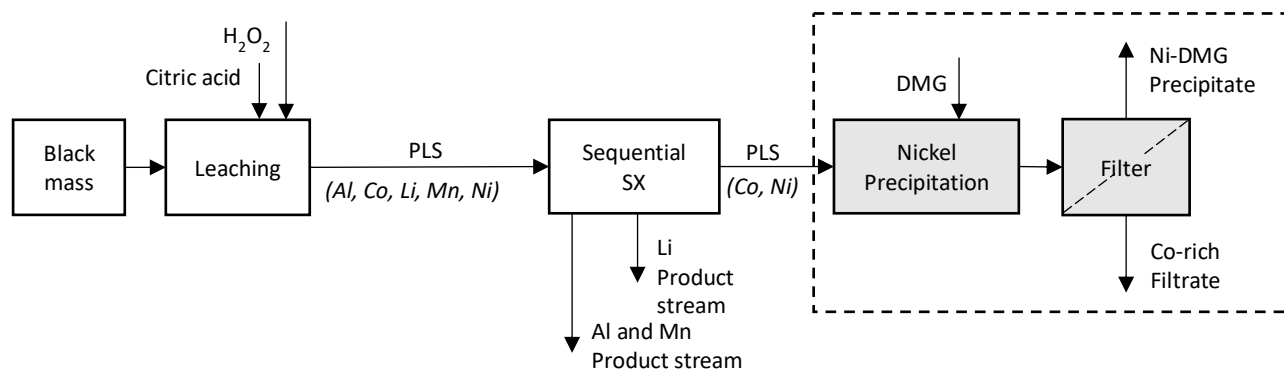


Figure 1. Proposed Ni-DMG precipitation after sequential solvent extraction.

EXPERIMENTAL

Materials and methods

The leach solution was prepared with a 99.8 wt.% anhydrous citric acid powder (CTA005) and 50 wt.% H₂O₂ (HPA002) supplied by KIMIX Chemicals and Lab Supplies. The feed stream for the precipitation batch tests was prepared using 95 wt.% D2EHPA (17723) purchased from Industrial Analytical, and kerosene (KER025L) supplied by KIMIX Chemical and Lab Supplies. The precipitation tests were performed with 99 wt.% dimethylglyoxime (162574) purchased from Sigma Aldrich. The pH was controlled with a 10M NaOH solution prepared from 98 wt.% NaOH pellets (SPL015) supplied by KIMIX Chemicals and Lab Supplies.

Equipment

The precipitation batch tests were performed in a 250mL beaker on a hot plate with magnetic stirring. A benchtop Hanna pH meter fitted with a H11310 pH probe in an overhead stand was used to measure the pH and temperature of the aqueous solution in the beaker. A watch glass was placed on top of the beaker before the experiment commenced to limit the evaporation of any liquid and prevent spilling under high stirring rates. After the experiment was completed, the contents of the beaker were poured onto filter paper placed in a vacuum filter to separate any precipitate from the solution. All aqueous samples were drawn with a syringe and pushed through a 0.45µm syringe filter into a sample tube. Aqueous samples were analysed with a Perkin Elmer Avio 500 ICP-OES.

Experimental procedure

Scrap 18650 LIB cells were used as feed material for this study. The cells were discharged in 5 wt.% NaCl, cut open with a bandsaw, and the cathodes were leached with 10 wt.% NaOH for two hours at 100g/L to obtain a fine black mass powder. An XRD analyses revealed that the black mass from the cathodes contained 84.2 wt.% LiNi_{0.45}Mn_{0.4}Co_{0.15}O₂ and 15.8 wt.% LiCoO₂. The black mass was leached with 1.5M citric acid and 2 vol.% H₂O₂ at 20 g/L and 95°C to obtain a realistic leach solution. The PLS was first treated with 12 vol.% D2EHPA and an O/A ratio of 2 at a pH of 2.5 to remove most of the aluminium and manganese present in the leach solution (Punt *et al.*, 2021). The novel solvent extraction process of Punt *et al.* (2021) was utilised thereafter to remove the lithium from the raffinate using 23 vol.% D2EHPA, O/A ratio 4, and pH 5.5 to produce a feed stream containing mostly cobalt and nickel for the precipitation tests in this study, as summarised in Table 1.

Table 1. Average metal concentration and standard error of precipitation feed stream

Metal	Al	Co	Li	Mn	Ni
Conc. (mg/L)	1.593 ±0.051	3135 ±6	296.8 ±0.8	148.6 ±0.2	3099 ±39

All precipitation batch tests were performed at 22°C±3°C for 30 minutes, as previous studies have illustrated the fast precipitation kinetics at room temperature (Chen and Zhou, 2014). A bulk volume of DMG was prepared for experiments to ensure the precipitant concentration is equal for all tests,

enabling better control of the Ni/DMG stoichiometric ratio. The DMG used for this study was dissolved in demineralised water. Drop-wise addition of 10M NaOH was required to improve the solubility of DMG and ensure that all DMG powder was dissolved. A 0.05M DMG solution was created for the precipitation tests at Ni/DMG ratios of 0.4 to 0.6, similar to that of previous studies (Chen *et al.*, 2015). A stronger 0.1M DMG solution was however created for the precipitation tests at Ni/DMG of 0.1 to 0.3 to reduce the precipitant volume required.

The precipitation batch tests performed for this study were all done by sampling the aqueous feed stream, summarised in Table , and adding the desired volume of the feed to a beaker. The beaker was placed on a magnetic stirrer and the pH probe was placed in the beaker using an adjustable overhead stand. The magnetic stirrer was set to 200 rpm while the aqueous feed stream pH was adjusted with a 10M NaOH solution. Once the desired pH was obtained, the precipitating agent was added to the beaker, the stirring was increased to 500 rpm, and the experimental time was started. The solution pH was measured continually and adjusted accordingly to ensure that the pH was kept within 0.1 of the equilibrium pH. The desired pH was maintained using a 1.5M citric acid solution to reduce the pH, while a 10M NaOH solution was used to increase the pH.

RESULTS AND DISCUSSION

The feed stream to the precipitation tests for this study was prepared from a realistic citric acid leach, which was treated with sequential solvent extraction processes. The near complete removal of Al and Mn in the first extraction and Li in the second extraction both require multiple counter current stages (Punt *et al.*, 2021). Due to the lack of specialised equipment to operate with multiple counter current stages on lab scale, the complete removal of Al, Mn, and Li could not be achieved within a single stage, which was used for the preparation of the feed stream. The composition of the feed stream to the precipitation, summarised in Table 1, therefore contains reduced quantities of Li and Mn, with dilute traces of Al. Due to the dilute quantities of Al present in the feed stream, the precipitation and analysis thereof was not included in this study.

Influence of Ni/DMG stoichiometric ratio

Figure 2 (a), (b), and (c) illustrate the metal precipitation as a function of the Ni/DMG ratio at a pH of 6, 7, and 8. It is known from the nickel precipitation reaction with DMG that the Ni/DMG stoichiometric ratio is 0.5 (Rath *et al.*, 2018), however, Figure 2 (a) to (c) illustrates that only 74% of the nickel is precipitated from the feed stream with an Ni/DMG ratio of 0.5. It was observed in Figure 2 that a Ni/DMG ratio of 0.2 or greater is required to precipitate more than 95% of the nickel from the feed stream, roughly 2.5 times the required stoichiometric ratio requirement.

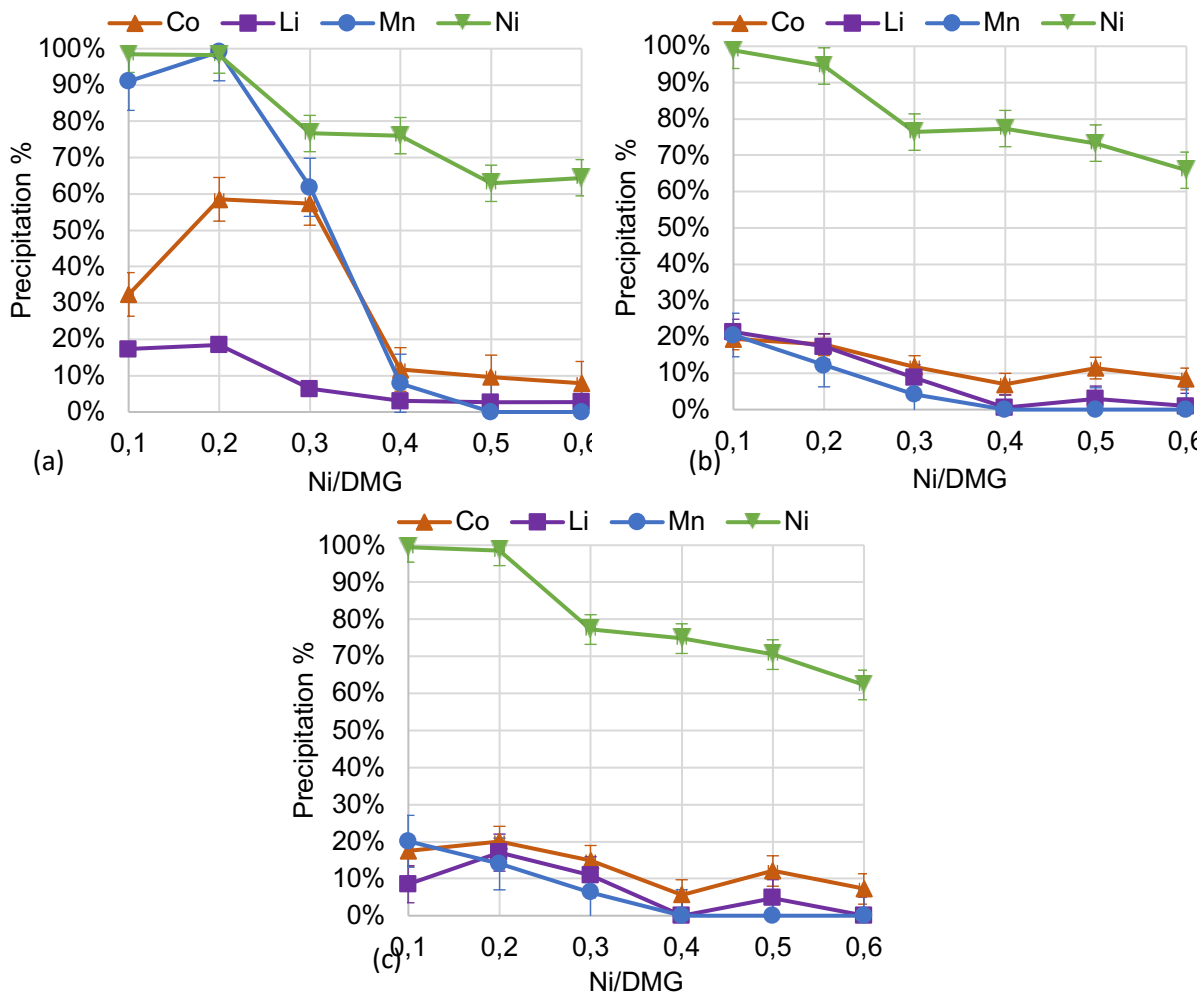


Figure 2. Nickel precipitation as a function of Ni/DMG ratios at a pH of (a) 6, (b) 7, and (c) 8.

As the Ni/DMG ratio is decreased below 0.4, the theoretical stoichiometric excess of DMG increases and leads to an increase in the co-precipitation of cobalt, lithium, and manganese as illustrated in Figure 2 (a) to (c) for Ni/DMG ratios of 0.4 to 0.1. This is due to excess amounts of the DMG reacting with the other metals to form stable metal compounds. Figure 2 (b) and (c) both show a gradual increase in the co-precipitation of cobalt, lithium, and manganese from under 10% to roughly 20% as the Ni/DMG ratio is decreased from 0.4 to 0.1, respectively. Figure 2 (a), however, shows a much sharper spike in the co-precipitation of cobalt, lithium, and manganese when the Ni/DMG ratio is decreased from 0.4 to 0.1, suggesting that the pH plays a significant role. The co-precipitation of metals with nickel must be reduced to maximise the nickel product stream purity and ensure that the filtrate contains the maximum amount of cobalt for a high overall cobalt recovery to the filtrate.

The stoichiometric excess DMG required for near complete nickel precipitation may be due to the superior stability of Ni-citrate complexes over Ni-DMG complexes, interference of citrate as a ligand, or potential irreversible Ni-citrate complexes that require a different precipitation reaction and stoichiometric ratio. It is thus recommended that future studies characterise the molecular structure of the Ni-DMG precipitate produced from citrate media. This will provide insight into the stoichiometric requirements and interference of the citrate ligand, including valuable information which may aid in the interpretation of the co-precipitation of cobalt, lithium, and manganese.

Influence of pH

The pH will affect the structure of the metal citrate complexes and the DMG in solution, influencing the solubility of the metal-DMG complexes and therefore their precipitation efficiency. Due to the poor nickel precipitation performance with DMG at Ni/DMG ratios of 0.4 and higher in Figure 2, the effect of pH was evaluated only for Ni/DMG ratios of 0.3 and less.

Figure 3 (a), (b), and (c) illustrate the metal precipitation as a function of pH for Ni/DMG ratios of 0.3, 0.2, and 0.1, respectively. It is apparent from Figure 3 that the nickel precipitation with DMG is not significantly affected by a change in pH between the range of 6 and 8, as the small variations in nickel precipitation over the pH range of 6 to 8 remained within the standard deviation error. This is likely due to nickel's strong affinity to DMG, which is unaffected within the pH range investigated. The strong affinity of DMG towards nickel is due to the divalent nature of nickel and its coordination number of 4, which enables bidentate DMG ligands to form stable tetrahedral Ni-DMG complexes containing 5-membered rings (Diehl, 1940).

It was also observed that the lithium precipitation with DMG was unaffected by changes in pH within the range of 6 to 8 for Ni/DMG ratios of 0.3, 0.2, and 0.1 in Figure 3 (a), (b), and (c), respectively. The lithium precipitation variance over the pH range of 6 to 8 for each Ni/DMG ratio investigated was larger compared to the variance of nickel in Figure 3 (a) to (c), but fluctuations also fell within the standard deviation error. The larger uncertainty associated with the lithium precipitation compared to nickel was attributed to variation in lithium concentration in the feed stream, which originated from variations in the performance of the lithium solvent extraction to produce the feed stream. Furthermore, the precipitation of lithium with DMG is not favoured as lithium is monovalent and its coordination number can vary greatly (Olsher *et al.*, 1991).

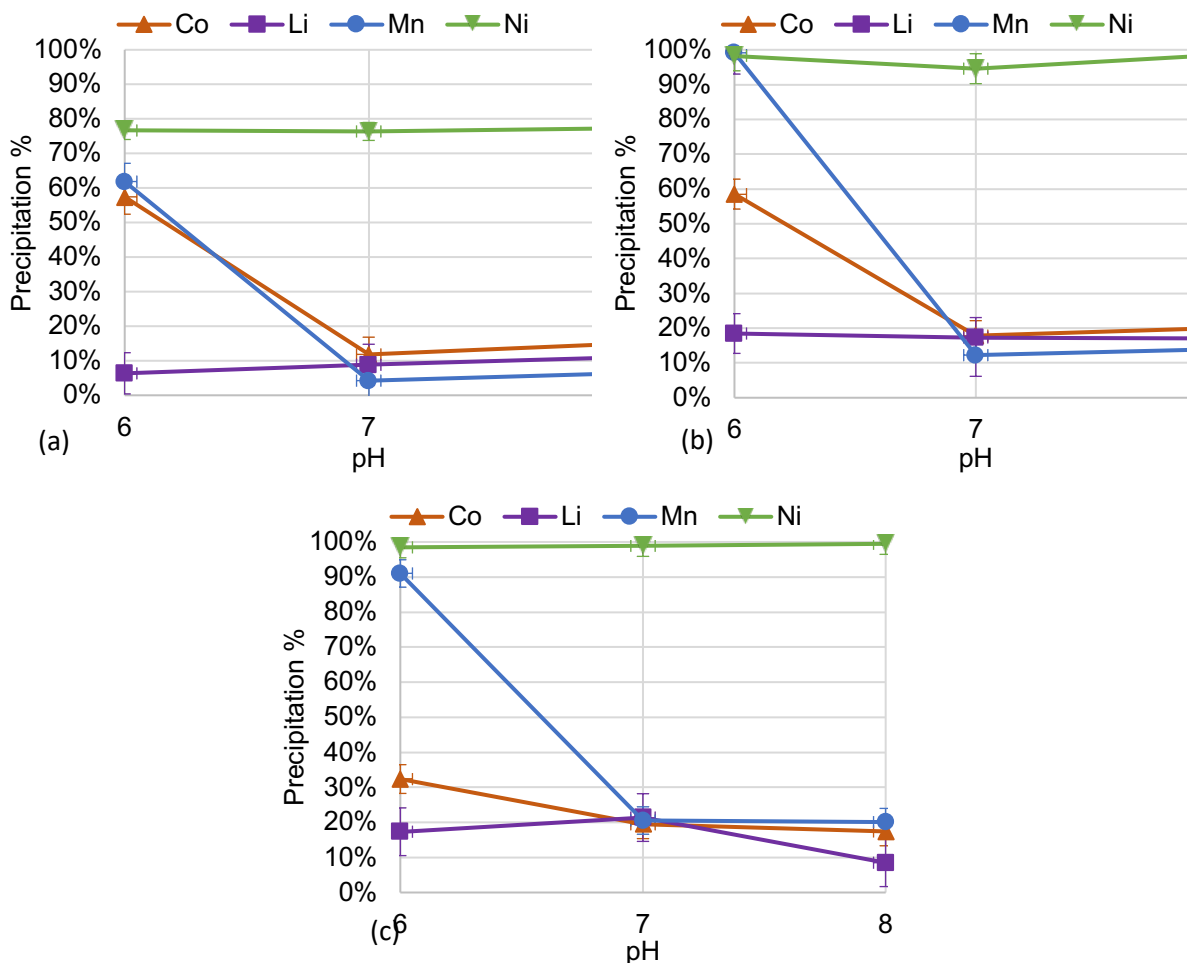


Figure 3. Nickel precipitation as a function pH for Ni/DMG ratios of (a) 0.3, (b) 0.2, and (c) 0.1.

The cobalt co-precipitation was observed to be greatly influenced by the pH for all Ni/DMG ratios investigated in Figure 3 (a) to (c). The cobalt co-precipitation remained unchanged as the pH decreased from 8 to 7 in Figure 3, after which the cobalt co-precipitation increased notably as the pH was decreased further from 7 to 6. The co-precipitation of cobalt is undesired, reducing the nickel product purity and limiting the cobalt recovery to the filtrate. The high cobalt co-precipitation at a pH of 6 was attributed to the reduced stability of cobalt in the citrate media under weak acidic conditions (Campi *et al.*, 1964), the divalent nature of cobalt(II), and the excess DMG introduced into the system.

Similarly, the manganese co-precipitation also remained unchanged between a pH of 8 and 7 in Figure 3. Decreasing the pH further to 6 leads to a significant increase in the manganese co-precipitation, where nearly complete manganese precipitation is achieved at a Ni/DMG ratio of 0.2 or 0.1 in Figure 3 (b) and (c), respectively. The high manganese co-precipitation was attributed to the weak stability of the Mn-citrate complexes (Li *et al.*, 1959), the divalent nature of manganese(II), and the octahedral co-ordination geometry of manganese(II) (Deng *et al.*, 2003; Wyrzykowski and Chmurzyński, 2010). It is therefore recommended that the Ni-DMG precipitation be performed at a pH of at least 7 to ensure that the cobalt and manganese co-precipitation is minimised, enabling the maximum nickel purity in the product.

Filtrate dilution

Precipitation plays a key role in metal recovery from hydrometallurgical processes to produce a reusable product. Nickel precipitation with DMG however provides an intermediary Ni-DMG precipitate product, which requires regeneration to enable the reuse of the expensive DMG precipitant in subsequent separations. It is therefore of utmost importance to ensure that the nickel precipitation with DMG has a minimal impact on the filtrate, as cobalt must be recovered from the filtrate in a

subsequent process. An inherent problem with chemical precipitation is that in order to induce the precipitation reaction, a precipitant must be added to the aqueous sample. In this study, a certain volume of DMG must be added to the feed volume to obtain the desired Ni/DMG ratio, increasing the total aqueous volume. The increased aqueous volume dilutes metals in the filtrate and increases the solubility of the metals in the aqueous, reducing the filtrate and precipitate quality.

Figure 4 illustrates the volume of feed and the 0.05M DMG precipitant used for Ni/DMG ratios of 0.4 to 0.6, with the associated cobalt dilution factor in the filtrate. It was observed that at a Ni/DMG ratio of 0.4, where a nickel precipitation of roughly 76% was achieved, the cobalt was diluted by a factor of around 4.5 to 5.1. This is undesired as the dilution of cobalt in the filtrate will complicate the cobalt recovery and greatly increase the process effluent volume, leading to increased process costs. A higher DMG precipitant concentration was therefore prepared to investigate the lower Ni/DMG ratios, which would require more DMG to be added to achieve the desired molar ratios.

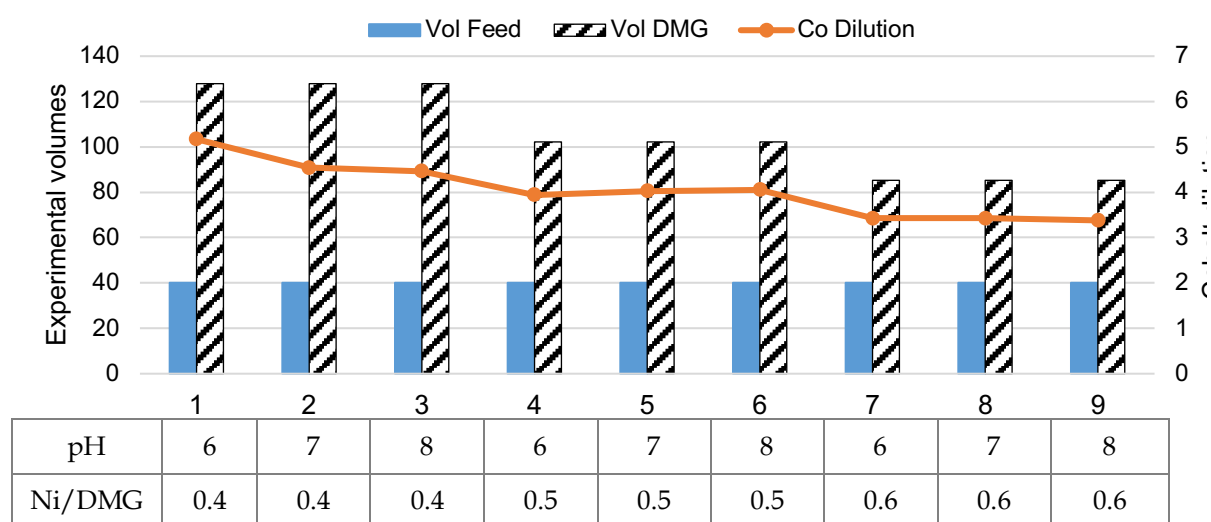


Figure 4. Metal dilution for 0.05M DMG precipitation.

The nickel precipitation with 0.1M DMG at Ni/DMG ratios of 0.1 to 0.3 is illustrated in Figure 5 with the cobalt dilution factor. It was observed that the cobalt dilution was much greater at a pH of 6 compared to the other pH levels at the same Ni/DMG ratio (see black data points). The increased dilution of cobalt in the filtrate at the pH 6 conditions in Figure 5 were thus determined to be due to the precipitant addition as well as the increased cobalt co-extraction observed at a pH of 6 for Ni/DMG ratios of 0.1 to 0.3 in Figure 2 and Figure 3. The increased DMG concentration notably reduced the cobalt dilution in the filtrate, as it was observed that at a Ni/DMG ratio of 0.2 and pH 8, where >98% nickel precipitation was achieved, the cobalt dilution in the filtrate was limited to 4.

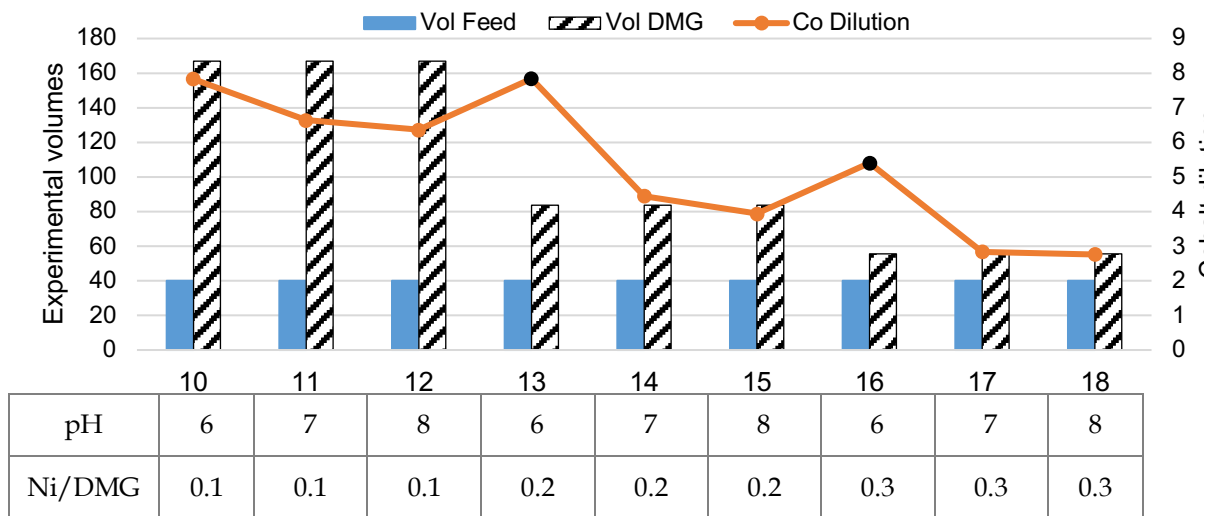


Figure 5. Metal dilution for 0.1M DMG precipitation.

It is therefore recommended that future studies aim to maximise the DMG precipitant concentration to minimise the impact of the nickel precipitation on the subsequent cobalt recovery from the filtrate. As the cobalt co-precipitation is reduced at higher pH levels, it would be possible to further increase the DMG precipitant concentration by adding more NaOH to the precipitant to dissolve the DMG.

Nickel precipitation optimisation

The nickel separation was optimised using three-dimensional wafer plots of the nickel precipitation and cobalt co-precipitation to determine which Ni/DMG ratio, and pH will enable the maximum nickel precipitation with minimal cobalt co-precipitation. The co-precipitation of lithium and manganese was not considered, as the metal separation process studied by Punt *et al.* (2021) removes nearly all the aluminium, manganese, and lithium by multi-stage counter current solvent extraction processes, and therefore this study prioritises the separation of nickel from cobalt.

Figure 6 illustrates the nickel precipitation as a function of pH and Ni/DMG ratio, where it is clear that the pH plays a minor role in the precipitation performance. It was observed in Figure 6 that a Ni/DMG ratio of at least 0.2 will be required to achieve >95% nickel precipitation. Further increasing the Ni/DMG ratio to 0.1 marginally increases the nickel precipitation efficiency but requires a significantly larger precipitant volume and leads to 1.6 times more dilution of cobalt in the filtrate.

Figure 7 illustrates the cobalt co-precipitation as a function of pH and Ni/DMG ratio. It is apparent from Figure 7 that pH has a significant influence on the cobalt co-precipitation, as a pH of 6 at Ni/DMG ratios of 0.3 and lower enable up to ~60% cobalt precipitation. It is thus recommended that the nickel precipitation be performed with a Ni/DMG ratio of 0.2 at a pH of 8, as indicated by the black filled data points on Figure 6 and Figure 7, where near complete nickel precipitation can be achieved with limited cobalt co-precipitation. Furthermore, a more concentrated DMG precipitant can be prepared at a higher pH to ensure that the cobalt dilution in the filtrate is limited.

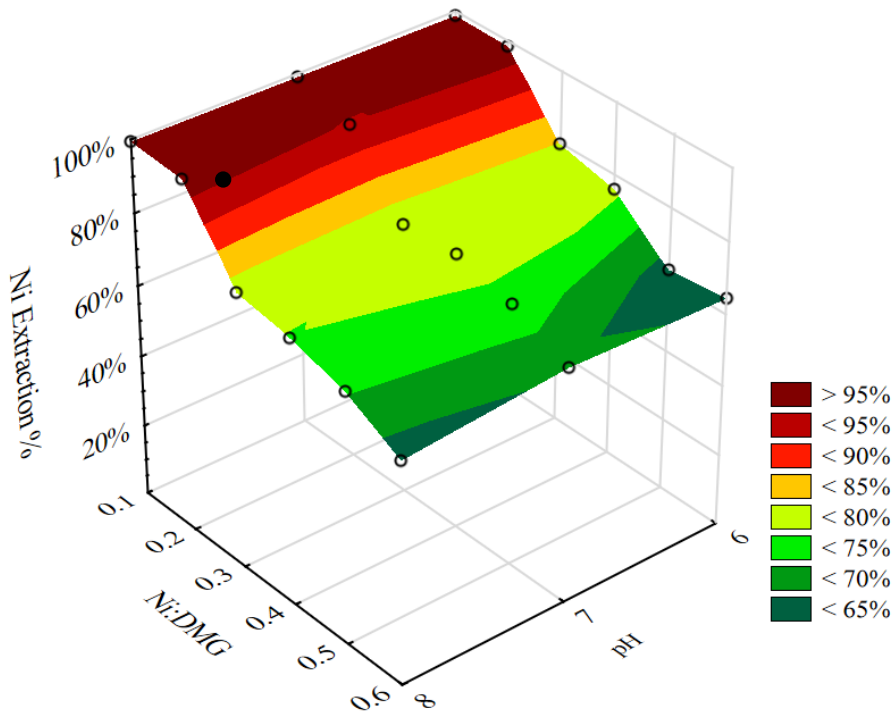


Figure 6. Nickel precipitation as a function of pH and Ni/DMG.

It is further recommended that the cobalt co-precipitation be investigated further to determine if the co-precipitation is due to adsorption, occlusion, mechanical entrapment, or substitution in crystal structure. If the cobalt co-precipitation is determined to be due to occlusion, the Ni-DMG precipitate can be washed and repulped to reduce the co-precipitation. If the cobalt co-precipitation is determined to be due to substitution in the crystal structure, the co-precipitation will have to be reduced by selectively stripping the cobalt from the Ni-DMG precipitate before recovering the nickel from the DMG with HCl to regenerate the DMG.

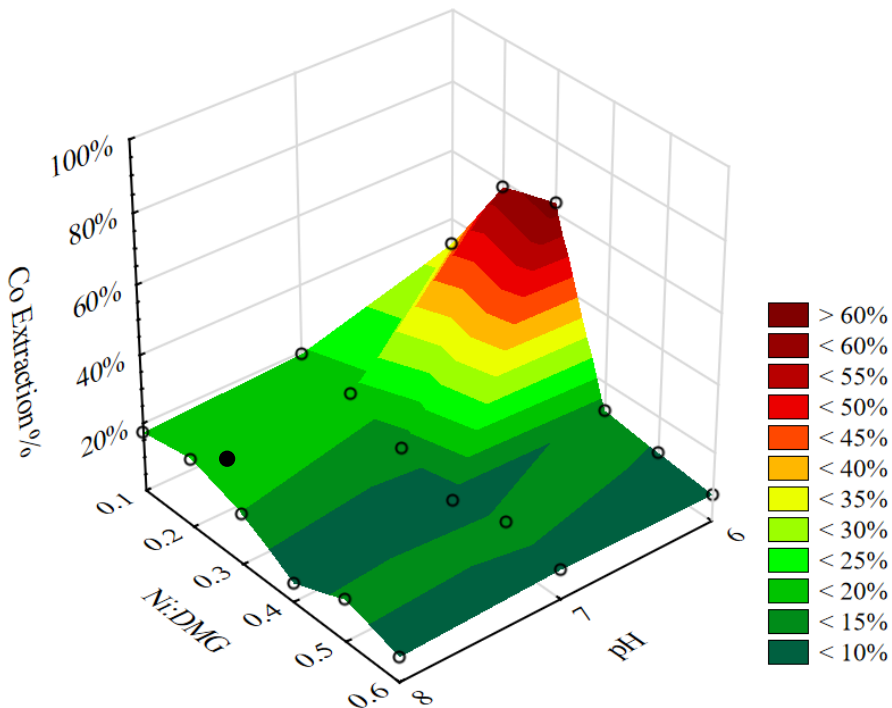


Figure 7. Cobalt precipitation as a function of pH and Ni/DMG.

CONCLUSIONS

Dimethylglyoxime (DMG) showed a strong selectivity towards nickel from the citrate lixiviant previously treated with solvent extraction to separate aluminium, manganese, and lithium. Initial tests indicated that the theoretical stoichiometric ratio of 0.5 was not sufficient for complete nickel precipitation. Further tests concluded that a Ni/DMG ratio of 0.2 was required for near complete nickel precipitation from the treated citrate lixiviant. A gradual increase in the co-precipitation of cobalt, and the residual lithium and manganese was however observed as the Ni/DMG ratio decreased.

The nickel precipitation efficiency was not significantly impacted by changes in the pH within the range of 6 to 8. The co-precipitation of cobalt and the residual manganese, however, increased notably when precipitation was performed at a pH of 6 and therefore it is recommended that precipitation be performed at a pH of at least 7 or greater. The co-precipitation of the residual lithium was poor and relatively consistent within a pH range of 6 to 8.

This study initially used a 0.05M DMG precipitant due to DMGs low solubility in water, which lead to the significant dilution of cobalt in the filtrate. The DMG precipitant concentration was successfully increased to 0.1M by increasing the pH of the precipitant using a 10M NaOH solution. This greatly limited the dilution of the cobalt in the filtrate, which must be recovered subsequently, ensuring a cobalt-rich filtrate, and reducing the process effluent.

It was concluded that the optimal nickel precipitation will be with a Ni/DMG ratio of 0.2 at a pH of 8, where 98.5% nickel is precipitated with roughly 20% cobalt. The near complete nickel precipitation produces a filtrate with a metal purity of 96.1% cobalt, enabling the recovery of a particularly pure cobalt product downstream. It is highly recommended that the cobalt co-precipitation be reduced with washing or selective stripping with a weak acid to reduce the co-precipitation as this will improve the nickel product purity and overall cobalt recovery.

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