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IRON REMOVAL PROCESS FROM NICKEL PREGNANT LEACH SOLUTION USING SODIUM HYDROXIDE

Mochamad Afriansyah Zunaidi[a,*], Iwan Setiawan[b], Soesaptri Oediyani[a], Januar Irawan[b], Ahmad Rizky Rhamdani[b], Adi Noer Syahid[b]
[a]Metallurgical Engineering, Faculty of Engineering, University of Sultan Ageng Tirtayasa
Jl. Jendral Sudirman Km.3, Cilegon, Banten, Indonesia 42434
[b]Research Center for Metallurgy, National Research and Innovation Agency
Management Building 720, B.J. Habibie Sains and Technology Area, Banten, Indonesia 15314
*E-mail: mochafriansyah@gmail.com

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Abstract

Indonesia is a country that has abundant mineral resources, including nickel resources in laterite ore. Nickel demand has risen significantly because of the need for nickel precursors for battery production. Nickel laterite can be processed via the hydrometallurgical route to obtain nickel precursor by leaching the laterite ore with an acid solution to produce a nickel-rich solution or PLS (pregnant leach solutions). This nickel-rich solution is then precipitated with a base solution to produce MHP hydroxides (mixed hydroxides precipitate). MHP is the primary product containing nickel and cobalt for the production of lithium battery material. PLS often contains iron impurities, which dissolve when the ore is leached. As a result, the iron must be separated in order to produce high-purity MHP. To address this issue, synthetic PLS with nickel, cobalt, and iron were created, and their concentration was simulated to match the general PLS composition. The experiment revealed that iron could be precipitated in two stages using 2.5 M NaOH solution at solution pH of 3 and 3.5. At a higher pH, nickel and cobalt can be precipitated. To investigate the effect of pH and temperature on the yield of nickel and cobalt precipitation, precipitation was carried out at pH 7, 8, and 9 and temperatures of 70, 80, and 90 °C. The results show that the highest yield was obtained at a pH of 9 and a temperature of 90 °C, with nickel and cobalt precipitation yields of 99.03% and 98.78%, respectively.

Keywords: *MHP (mixed hydroxide precipitate), iron removal, pH, temperature, precipitate*

1. INTRODUCTION

Indonesia is a country that has a wealth of natural resources and abundant mineral resources [1]. Many minerals have the potential to transform into nickel, such as sulfide compounds and oxide compounds (laterite ores) [2]. However, the dwindling amount of nickel sulfide reserves can be a problem to face in the future. Therefore, it is necessary to use laterite as a nickel source, although laterite ore contains lower nickel content than sulfide ore. Laterite nickel processing can be carried out through pyrometallurgical or hydrometallurgical processes [3]. In the nickel processing industry, hydrometallurgical nickel ore processing lines include the Caron Process, HPAL (high-pressure acid leaching), AL (agitation leaching), and HL (heap leaching) [4].

The intermediate product from the leaching process is usually called a PLS (pregnant leaching solution). The PLS is then processed by precipitation method to produce the final product, generally in the form of a MHP (mixture of hydroxide precipitate) or a MSP (mixture of sulfide precipitation). The PLS from the leaching process could also be processed before the precipitation process via a solvent extraction route to separate the dissolved metal into a different solution to produce higher-purity PLS [5]-[6]. MHP is a commercially proven technique [7]; MHP has a nickel content of around 3,8%-34%, while MSP is about 55%. MHP has received a lot of attention because it has several

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advantages over the MSP method, such as easier precipitation to obtain nickel and cobalt as concentrates and a more accessible nickel and cobalt extraction process [8]-[9]. However, obtaining MHP precipitate with high nickel and cobalt content is challenging because there are too many impurities.

In this study, the MHP precipitation method was used, which previously carried out an iron removal process so that the precipitated nickel and cobalt could be free from iron compounds [10].

2. MATERIALS AND METHODS

The synthetic PLS (pregnant leaching solution) was prepared by first diluting a certain amount of nickel sulfate hexahydrate, cobalt sulfate heptahydrate, and iron sulfate separately in aquademin in an acidic condition. The solutions were mixed and diluted with aquademin to get 5 liters of PLS. The synthetic PLS was taken as much as 5 ml and diluted in a volumetric flask up to 100x dilution to be analyzed for elemental content using ICP-OES (inductively coupled plasma-optical emission spectrometry). Then the iron removal process was carried out using 2.5 M NaOH with a two-step process where the first stage was carried out until the pH of the solution reached 3 and the second stage until the pH of the solution got 3.5. Each of these stages is conducted for 1 hour. Then, the MHP (mixed hydroxide precipitate) precipitation process was carried out for 1 hour with temperature variations of 70, 80, and 90 °C and pH variations of 7, 8, and 9.

The obtained MHP was then dried at 110 °C for 6 hours in an oven. Furthermore, the MHP formed was weighed using a digital balance and analyzed using XRF (x-ray fluorescence) S2 PUMA to determine the elemental composition in the mixtures. XRD (x-ray diffraction) Shimadzu type 7000 analysis was carried out to determine the phases, and SEM (scanning electron microscope) analysis was also conducted to determine the morphology of the nickel hydroxide formed.

3. RESULT AND DISCUSSION

The experiment was conducted using a synthetic mixture of nickel sulfate hexahydrate, cobalt sulfate heptahydrate, and iron (III) sulfate in this study. The solution was created with a Fe, Ni, and Co ratio of 30:20:1. The synthetic PLS (pregnant leaching solution) was created by dissolving 267.86 g of ferric sulfate, 222.74 g of nickel sulfate hexahydrate, and 11.91 g of cobalt sulfate heptahydrate in 5 L of 0.2 M sulfuric acid to yield PLS with iron concentrations of 15 g/L, 10 g/L, and 0.5 g/L, respectively. The conditions for making this synthetic PLS solution adopted the research conducted by Topkaya [12], which carried out multi-step leaching of nickel limonite ore using a leaching agent in the form of sulfuric acid with nickel extraction in the range 85%-89%, cobalt extraction about 57%-71% and iron extraction around 68%-79%. Furthermore, the AAS (atomic absorption spectrometry) instrument first analyzed the PLS to determine the actual concentration of iron, cobalt, and nickel in the process, and the results are listed in Table 1.

Table 1. AAS analysis for synthetic PLS

Element	g/L
Nickel (Ni)	9.488
Cobalt (Co)	0.4937
Iron (Fe)	11.91

The iron removal process was carried out in two stages by adding 2.5 M NaOH at 80 °C and stirring at 450 rpm for 1 hour. In the process of iron removal stage 1; 45 mL of 2.5 M NaOH was added to 200 mL PLS until the pH in the solution was up to 3. The result from the iron removal process stage 1 is that iron could be selectively precipitated in the process. The iron concentration in the PLS after stage 1 could be reduced up to 99.53%, with nickel and cobalt concentration only slightly reduced to 1.265% and 0.546%, respectively. For the process of iron removal stage 2; 15 mL, NaOH 2.5 M was added to the solution to raise the pH to 3.5. The accumulated reduction value of iron concentration in the PLS from stages 1 and 2 is 99.95%, with the concentration of nickel and cobalt only decreasing by 1.311% and 1.357%, respectively. The primary purpose of the iron removal process is to neutralize acid and precipitate iron as much as possible because iron is the impurity with the highest content in PLS.

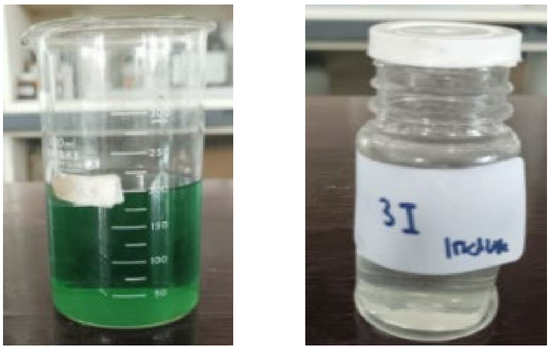
3.1 Color Change in the Precipitation Process

In the MHP (mixed hydroxide precipitate) precipitation process, several phenomena were observed, such as a color change from light green to transparent, as shown in Fig. 1.

Table 2. Results of ICP-OES analysis of PLS solution after precipitation of MHP

Element	g/L
Nickel (Ni)	0.9234
Cobalt (Co)	0,0006

Figure 1 depicts the color changes experienced by the solution prior to and after the MHP precipitation process. This color change indicates that a lot of nickel and cobalt contained in the PLS solution have been precipitated so that the solution only had a small amount of nickel and cobalt, as shown in Table 2.



(a) (b)

Figure 1. (a) PLS before MHP precipitation process, (b) PLS after MHP precipitation process

3.2 Precipitation of MHP with Various Temperature

One of the factors that can influence the MHP precipitation process is temperature. Temperature variations were carried out in the MHP precipitation process at 70, 80, and 90 °C with a precipitation time of 3 hours and added NaOH 2.5 M 45 mL, 15 mL, and 5 mL, respectively.

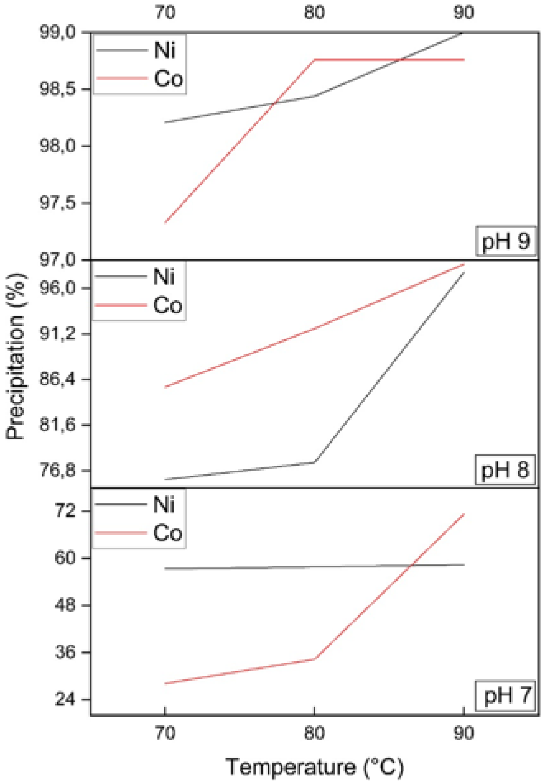


Figure 2. Effect of temperature on element precipitation

The results show that at 70 °C, the lowest nickel and cobalt content precipitated in the MHP was 57.86% and 29.11%, respectively. At 90 °C, the highest value of nickel and cobalt content precipitated was 99.014% and 98.768%, respectively. The relationship between nickel and cobalt content deposited on MHP can be seen in Fig. 2.

Based on Figure 2, it can be seen that the nickel and cobalt deposited in the MHP increased with increasing temperature. The higher the temperature of the precipitation process, the higher the recovery of nickel and cobalt precipitated [12]. The higher the temperature used, the higher the kinetic energy of the molecules of substances in the solution that will react so that the more molecules of substances that have energy more significant than the more signification energy, the more effective collisions occur, which will increase the reaction rate [12]. The higher the reaction rate, the faster the reaction will occur, so more nickel and cobalt will precipitate [11]. Based on the data obtained, it can be seen that temperature influences the MHP precipitation process, with the optimum temperature obtained at 90 °C.

3.3 Precipitation of MHP with Various pH

This research was also carried out with pH variations in the MHP precipitation process.

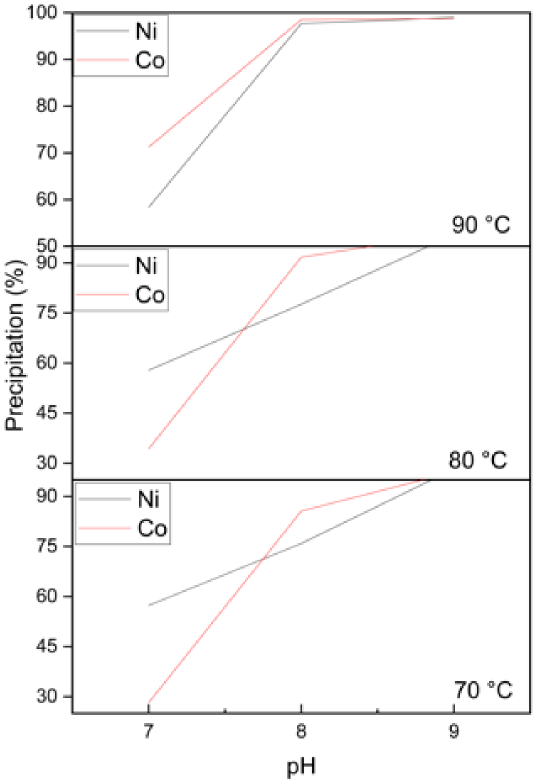


Figure 3. Effect of pH on element precipitation

With a precipitation time of 3 hours, the pH variations used were 7, 8, and 9. According to the research findings, the lowest nickel and cobalt content in the precipitate was obtained at pH 7, 57.86% and 29.10%, respectively. The highest nickel and cobalt concentrations in the precipitate were obtained at pH 9, namely 99.02% and

98.78%, respectively. If the pH variation is plotted against the nickel and cobalt precipitates recovery, a curve is shown in Fig. 3.

Based on Figure 3, it can be seen that the value of nickel and cobalt deposits in MHP increases with increasing pH. The higher the pH used, the higher the recovery of nickel and cobalt deposits; this is to research conducted by Oustadakis et. al., [12] which showed that increasing pH resulted in more significant precipitation of metal hydroxides.

3.4 XRF (X-Ray Fluorescence) Analysis on MHP (Mixed Hidroxide Precipitate)

The result of XRF (x-ray fluorescence) analysis of MHP residues at pH 9 and a temperature of 90 °C can be seen in Table 3. XRF analysis was conducted to determine the levels of nickel and cobalt formed after the MHP precipitation process. The result has a low Fe content because the iron was removed first in the previous processes. These results show that the nickel and cobalt content of the produced MHP is very high, while the iron content is very low. The iron content in the MHP XRF analysis indicates that the iron removal process was successful in removing the majority of the Fe in the solution.

Table 3. XRF Analysis for MHP synthesized a pH of 9 and temperature of 90 °C

Element	Wt.%
Nickel (Ni)	61.467
Cobalt (Co)	1.560
Ferum (Fe)	0.003

3.5 XRD Analysis on MHP (Mixed Hydroxide Precipitate)

MHP compounds were also analyzed using XRD to determine the nickel and cobalt compounds formed after the MHP precipitation process.

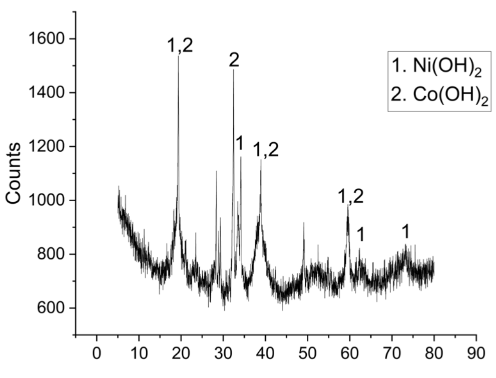


Figure 4. X-ray diffraction pattern for MHP (mixed hydroxide precipitate)

The XRD diffraction pattern was analyzed with the ICSD (inorganic crystal structure database) standard using the HSP (high score plus) software to identify $Ni(OH)_2$ and $Co(OH)_2$ compounds. The tested samples obtained that the comparison image of the X-ray diffraction pattern of the experimental MHP samples had similarities with the x-ray diffraction pattern based on the ICSD No. Standard. 98-002-4015 and ICSD No. 98-008-8940, the diffraction pattern of $Ni(OH)_2$ and $Co(OH)_2$ compounds. The XRD analysis was carried out with the range of 2θ angle of 10°-80°. The sample found typical peaks of Ni(OH)2 at 2θ (°) = 19, 33, 38, 52, 59, 62 and 70 and found peaks of Co(OH)2 at 2θ (°) = 19, 32, 38, 51, 58, 61 and 69. The higher the peak produced, the more compounds formed. Figure 4 shows a comparison image of x-ray diffraction at MHP, the result of precipitation at pH 9, and a temperature of 90 °C.

3.6 SEM (Scanning Electron Microscope) Analysis on $Ni(OH)_2$

The results of the SEM (scanning electron microscope) analysis of the MHP are illustrated in Fig. 5. SEM micrographs show that the formation of nickel hydroxide particles occurs through the aggregation of small particles. The incorporation mechanism of growing nickel hydroxide crystals has also been studied previously by Jones [13]. Elemental mapping in MHP is carried out to determine the compounds in MHP through SEM-EDS (energy dispersive spectrometry) analysis (Fig. 6).

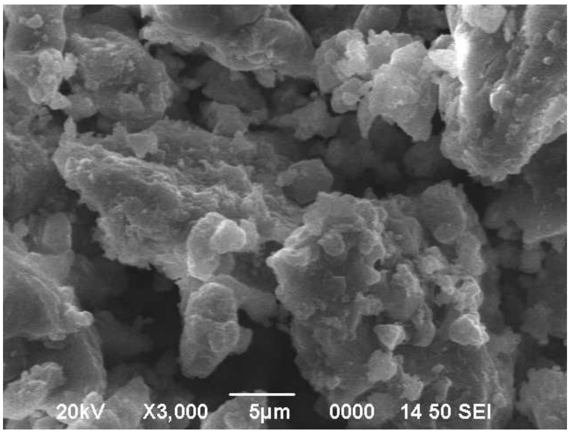
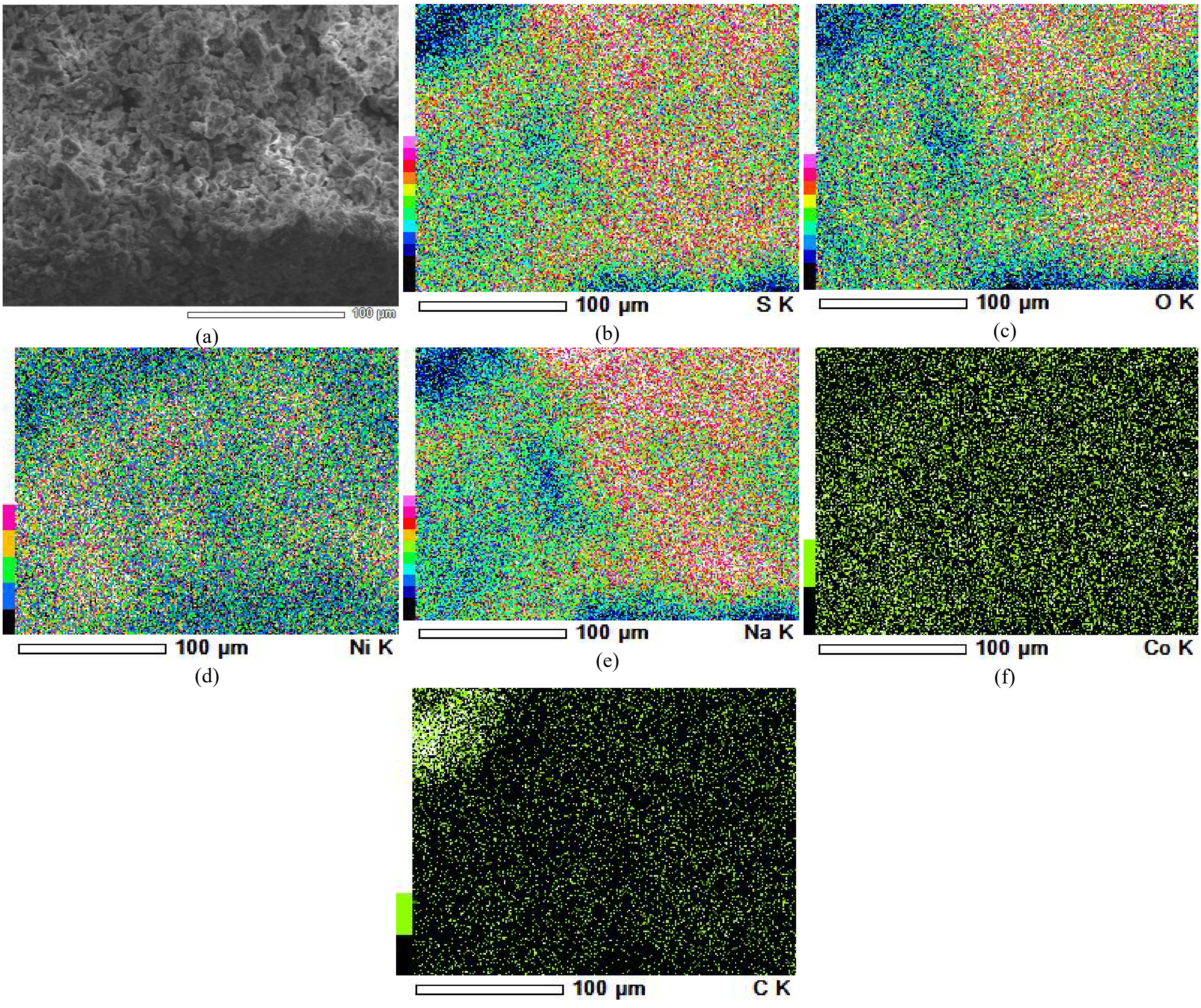


Figure 5. Morphology of $Ni(OH)_2$ at 90 °C temperature and pH 9

Several points on the MHP indicate the presence of sodium as the main impurity in the precipitate. The presence of sodium in the form of sodium ulfate produced by the reaction of sodium hydroxide as a pH regulator and sulfuric acid was also detected and can be seen in Fig. 6.

3.7 Mass of Mixed Hydroxide Precipitate

The nickel and cobalt content precipitated in MHP (mixed hydroxide precipitate) was weighed based on the study results. The highest sediment mass gain was obtained at pH 9 at 90 °C with a precipitate mass of 5.61 grams, while the lowest sediment mass was obtained at pH 7 at 70 °C with a sediment mass of 1.12 grams.



(a) (b) (c)

(d) (e) (f)

(g)

Figure 6. (a) BSE image of MHP at 90 ºC temperature and pH 9 with EDS elemental mapping of (b) Sulphur, (c) Oxygen, (d) Nickel, (e) Natrium, (f) Cobalt, and (g) Carbon

This result shows that the higher the pH and temperature, the higher the MHP precipitate obtained. Nickel content was obtained at optimum conditions, namely pH of 9 and temperature of 90°C, with a nickel content in MHP of 33.49% and cobalt of 1.738%. The results of the MHP mass measurement are then plotted in Fig. 7.

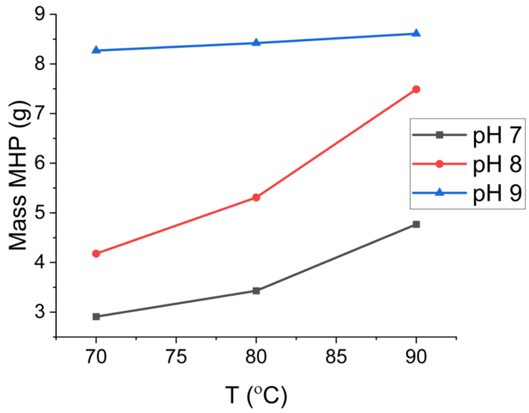


Figure 7. MHP (mixed hydroxide precipitate) mass after Ni/Co precipitation

4. CONCLUSION

This work successfully removed iron from PLS (pregnant leach solution) through two stages of precipitation. The first stage was conducted at pH of 3 and the second stage at pH 3.5. After two stages of precipitation, 99.95% of iron could be removed. The nickel and cobalt which co-precipitated in the iron removal process is only 1.311% and 1.357%, respectively, indicating that the iron removal process is selective.

Nickel and Cobalt then could be precipitated in the form of MHP (mixed hydroxide precipitate) at pH of 9 and 90 °C. The maximum value of nickel and cobalt precipitation yield are 99.03% and 98.78%, respectively. The content of nickel and cobalt in the resulting MHP are 33.49% for nickel and 1.734%, respectively.

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