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Recovery of nickel from spent electroplating solution by hydrometallurgical and electrometallurgical process

Piamsak LAOKHEN[1], Natthicha MA-UD[1], Tanongsak YINGNAKORN[1], Tapany PATCHARAWIT[1], and Sakhob KHUMKOA[1,*]

[1] *School of Metallurgical Engineering, Institute of Engineering, Suranaree University of Technology, Suranaree, Muang, Nakhon Ratchasima 30000, Thailand*

***Corresponding author e-mail:** sakhob@sut.ac.th

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Abstract

Recovery of nickel from spent electro nickel plating solution has been investigated via hydrometallurgical and electrometallurgical processes. Experimental consisted of 3 steps, including precipitation of nickel from spent solution, leaching of nickel precipitate, and electrowinning of nickel. Nickel precipitation was performed using sodium hydroxide. Leaching parameters such as 1 M to 3 M sulfuric acid concentration, 100 $g\cdot L^{-1}$ to 300 $g\cdot L^{-1}$ solid to liquid ratio, and 30 min to 180 min leaching time were investigated. The leachate from the optimal leaching condition was further used as an electrolyte in electrowinning process. Effects of 3.3 V to 3.7 V cell voltage on recovery and purity of nickel and current efficiency of the electrowinning process were investigated. The results showed that nickel precipitation could be performed by using 2 M sodium hydroxide to adjust the solution to pH $\geq$13. For leaching, dissolution of nickel precipitate of higher than 90% was achieved at the optimum leaching condition of 2 M sulfuric acid, solid to liquid ratio of 100:1 $g\cdot L^{-1}$ and leaching time of 60 min. Electrowinning of nickel applying the cell voltage of 3.5 V for 24 h showed the greatest nickel recovery of about 61%, giving nickel purity of 99% while the current efficiency of electrowinning cell of approximately 16% can be achieved.

1. Introduction

Environmental pollution is one of the most serious problems that humanity has to encounter today. Such problems might have accumulated till present and that will be certainly becoming more difficult to solve in the future if no measures have been taken [1]. In some countries, such as in the United States, European countries, Japan, electrical and electronics equipment waste management schemes have been undertaken with firm environmental legislations [2]. In addition, modern technology has evolved over the years where electrical and electronic industries along with those in the automotive part areas have gained much attention with significant growth in the market [3]. To serve the aforementioned industries, the supply chain such as metal finishing is essentially important and liable for environmental issues. In metal plating, hazardous wastes generated from most operations specifically the electroplating operation along with waste water treatment in the rinsing steps where heavy metals for example, nickel, copper, zinc and cobalt involved are considered hazardous [4]. Spent electroplating solution therefore requires proper treatment prior to disposal especially when it still contains significant amounts of valuable metals up to about 90 $g\cdot L^{-1}$. It is more worthy to make it through the recycling route in order to reduce the impact of hazardous waste while increasing the economic value of the metals involved [5].

Nickel plating is commonly used worldwide as it offers good strength, toughness and corrosion resistance with cost effective [6]. The spent nickel plating solution can be recovered via regeneration for reuse in the process and also recovered as nickel of high purity along with other valuable metals. The latter concerning recovery of nickel from the spent plating solutions has gained notable interest through many research studies and newly developed technologies. With the intention of recovering nickel from the solution, hydrometallurgy is the most suitable for both time-saving and expecting metals of high-purity. The key methods involved are chemical precipitation, ion flotation, ion-exchange, membrane filtration, adsorption, continuous solvent extraction, and electrochemical treatments such as electrodialysis, electrowinning and electrorefining [7-12]. In the electrowinning process, nickel in the solution is extracted and deposited as nickel metal at cathode. There are many factors affecting the quality of nickel deposit, such as current density, conductivity, pH and temperature [13-15]. Research by H. Y. Lee *et al.* [14] studied the effects of nickel recovery from an electroless nickel plating solution by using precipitation, leaching and electrowinning methods. Their result indicated high nickel recovery of 62.5% and current efficiency of 37% can be achieved when using current density at 80 $mA\cdot cm^{-2}$ in the last step of electrowinning. Fine nickel precipitate of less than 4 μm size was obtained when adjusting the spent electroless plating solution to pH $\geq$ 13 using caustic soda, followed by dissolution

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in sulfuric acid and electrowinning at a precise pH equals 2. However, important factors affecting leaching of nickel precipitate has not been explored. It is therefore of interest to further develop such techniques in order to recover nickel and/or other heavy metals from the waste solutions and to refine the related leaching parameters in order to obtain optimum leaching condition for effective electro-winning in the final step.

The purpose of this research is thus to extract nickel metal from waste electroplating solution by using spent electro nickel plating solution obtained from domestic nickel plating industry. The recycling route started with precipitation of nickel and then leaching to various variables of interest such as acid concentration, solid to liquid ratio and time. The nickel metal was then extracted by the electrowinning at various electric potential values.

2. Experimental

2.1 Materials

The spent electro nickel plating solution was obtained from domestic nickel plating industry for the manufacturing of grinding and cutting-edge devices. Analyzed by ICP-OES technique, waste composition showed significant amounts of nickel and other elements remained in the solution, as listed in Table 1, where the average amount of nickel is 133 $g\cdot L^{-1}$. There are other minor elements such as aluminium of 146 $mg\cdot L^{-1}$, phosphorus of 79.0 $mg\cdot L^{-1}$ and copper of 3.54 $mg\cdot L^{-1}$.

2.2 Method

The experiment can be divided into 3 main steps, i) nickel precipitation, ii) acid leaching of nickel precipitate, and iii) nickel extraction via electrowinning, as illustrated in Figure 1. In the process of nickel precipitation, sodium hydroxide (NaOH) solution was utilized for precipitation so that the pH of the solution approached an approximate value of 13. The nickel precipitate was then dried to get rid of moisture and crushed into a smaller size in order to improve leaching efficiency in the later step by increasing its surface area. In the second step of acid leaching, effects of sulfuric acid concentrations at 1.0, 2.0 and 3.0 M were studied while using solid to liquid (S/L) ratio of 100 $g\cdot L^{-1}$ and leaching time for 60 min. After the leached solution was analyzed by ICP-OES, the optimum acid concentration was determined. Then from the selected optimum condition of acid concentration, variations of solid to liquid ratio at 100, 200 and 300 $g\cdot L^{-1}$ for 60 min and varied leaching time at 30, 60, 90, 120, 150 and 180 min were studied. The leached solution was then analyzed for nickel and other metal concentrations by ICP-OES technique such that % leaching of nickel could be calculated and impurity amounts remained in the solution were determined.

In the last step of electrowinning, the leached solution obtained via optimum condition to give high nickel content with low levels of impurities was selected. Based on electrolytic cell set up as demonstrated in Figure 2, the leached solution was utilized as an electrolyte solution, using platinize-titanium as the anode and 304 stainless steel sheet 5 cm long by 5 cm wide, and 1 mm thick as the cathode. The electrowinning experiments were performed at ambient temperature and the electrolyte was agitated using magnetic stirrer at a rotation speed of 200 rpm. By applying the electric current from a DC power supply through the cell for 24 h, principally the negative ions or electron moves corresponding to the movement of positive ions (Ni^{2+}) in the solution to accumulate at the cathode as the desired recycling product. Electrical potential of 3.3, 3.5 and 3.7 V, which is corresponded to the initial current density of 0.9, 1.5, and 2.1 $A\cdot dm^{-2}$, respectively, were investigated. As the electrowinning experiment finished, the electrolyte was filtered to separate out some residue and precipitates remained at the bottom of the container. Chemical compositions of the nickel cathode and electrolyte were analyzed by ICP-OES technique to determine % recovery and % current efficiency (ε) of electrowinning process by applying the mathematic expressions in equation (1) and (2) respectively as follow;

$$\% \text{ Recovery} = [(C_i - C_f)/C_i] \times 100 \tag{1}$$

$$\% \text{ Current efficiency } (\varepsilon) = [W/(ItA/zF)] \times 100 \tag{2}$$

Where C_i and C_f are the initial and final concentrations of nickel, W is the weight deposited in gram, I is the current used in ampere, t is electrowinning time in second, A is the atomic weight in gram, z is the electrochemical equivalent, i.e., weight deposited in gram when passing 1 ampere current for 1 s, and F is the Faraday's constant.

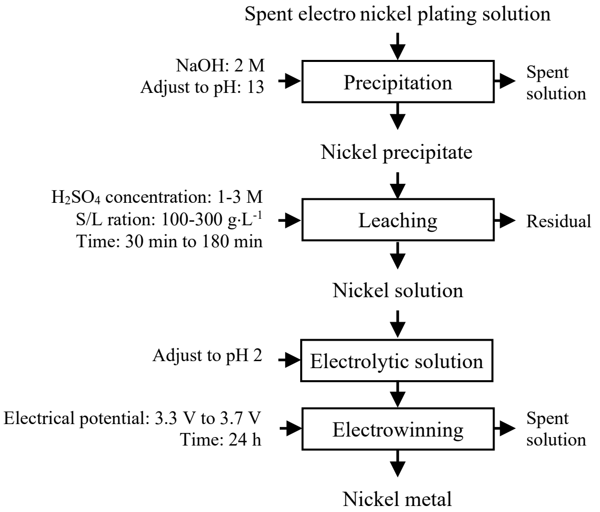


Figure 1. Experimental flow chart of nickel recovery via hydroelectro metallurgical process.

Table 1. Chemical analysis of spent electro nickel plating solution by ICP-OES.

Element	Ni	Cu	Fe	Pb	P	Al
Concentration ($mg\cdot L^{-1}$)	133,100	3.54	0.718	0.323	79.10	146.00

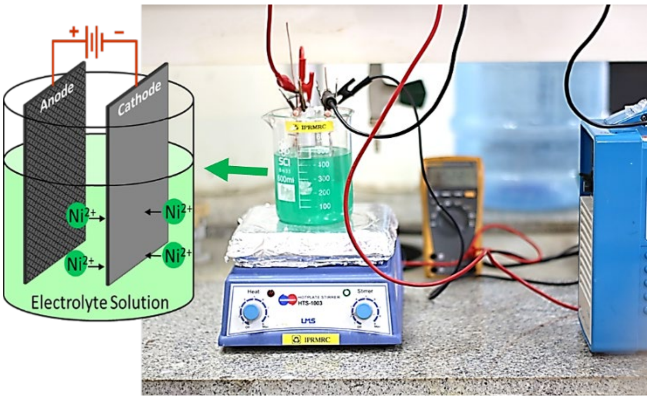


Figure 2. Electrochemical cell set up for nickel recovery from nickel solution.

3. Results and discussion

3.1 Effects of sulfuric acid concentration on nickel leaching and amount of dissolved metals in leachate

After the spent nickel plating solution was subjected to precipitation by adjusting the pH ≥ 13, the obtained precipitate in the form of nickel hydroxide ($Ni(OH)_2$) was filter rinsed and subjected to sulfuric acid leaching. The chemical reaction of nickel hydroxide leaching with sulfuric acid can be expressed by equation (3).

$$Ni(OH)_{2\,(s)} + H_2SO_{4(aq)} \rightarrow NiSO_{4(aq)} + 2H_2O_{(aq)} \qquad (3)$$

By considering leaching at solid to liquid ratio of 100 g·L^{-1} for 60 min, increasing sulfuric acid concentration has showed to affect nickel leaching efficiency as illustrated in Figure 3. As the acid concentration raised from 1.0, 2.0 and to 3.0 M, the nickel leaching efficiency slightly increased to 90.75%, 91.96% and 92.78% respectively. On the other hand, dissolution of impurities such as aluminium, phosphorus, iron and lead were found to decrease with increasing leachant concentration as shown in Figure 4. Since sulfuric leaching is very selective for nickel, increasing acid concentration thus resulted in higher nickel leaching efficiency while other metals have gone to the sediments which were not leached.

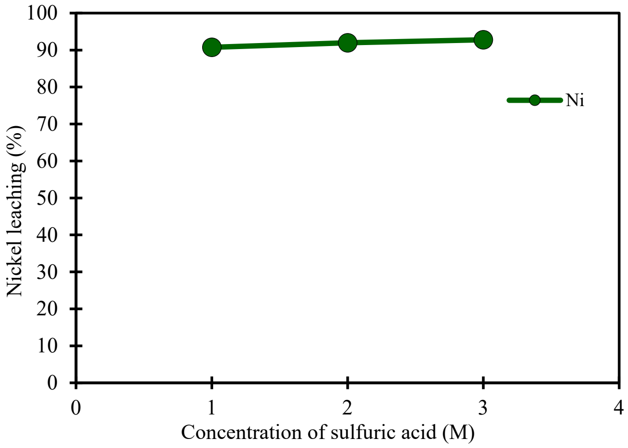


Figure 3. Effects of sulfuric acid concentration on nickel leaching (leaching condition: 100:1 g·L^{-1} solid/liquid ratio, 60 min leaching time).

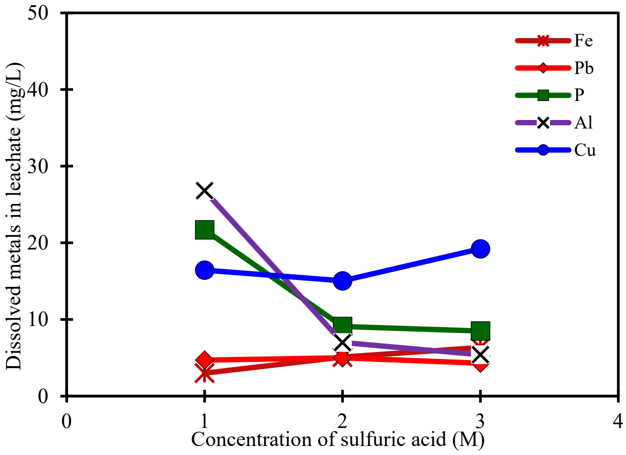


Figure 4. Effects of sulfuric acid concentration on amount of dissolved metals in leachate (leaching condition: 100:1 g·L^{-1} solid/liquid ratio, 60 min leaching time).

3.2 Effects of the solid to liquid ratio on nickel leaching and amount of dissolved metals in leachate

As the solid to liquid ratio is another important factor affecting the leaching efficiency, its effects have been studied in the range of 100 g·L^{-1} to 300 g·L^{-1} at a fixed condition of 2 M sulfuric acid concentration and leaching time of 60 min. It was found that when the solid to liquid ratio increased from 100 g·L^{-1} to 200 g·L^{-1} and 300 g·L^{-1}, leaching of nickel tended to decrease from 91.96% to 90.47% and 84.78% respectively as demonstrated in Figure 5. Meanwhile, the dissolution of impurities increased as the ratio of solid to liquid increased, as illustrated in Figure 6. It can be seen that at the fixed acid concentration of 2 M, the solubility has changed with increasing the solid to liquid ratio. The amount of the acid used was not sufficient to leach the nickel metal at greater solid content. Then by using high solid to liquid ratio, high metal content could not be leached completely. It however appeared that with increasing solid to liquid ratio, nickel leaching has reduced while the impurity elements on the other hand can be further leached. It might be that the concentration of the remaining solution cannot continue to leach the nickel but instead it was capable of leaching other impurities in the sediment.

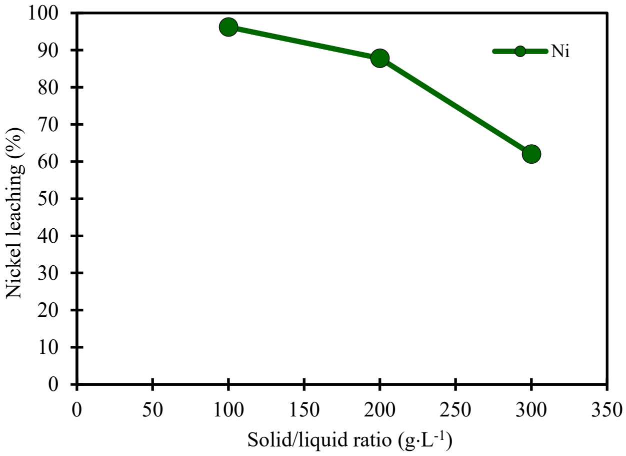


Figure 5. Effects of solid/liquid ratio on nickel leaching (leaching condition: 2 M sulfuric concentration 2 M, 60 min leaching time).

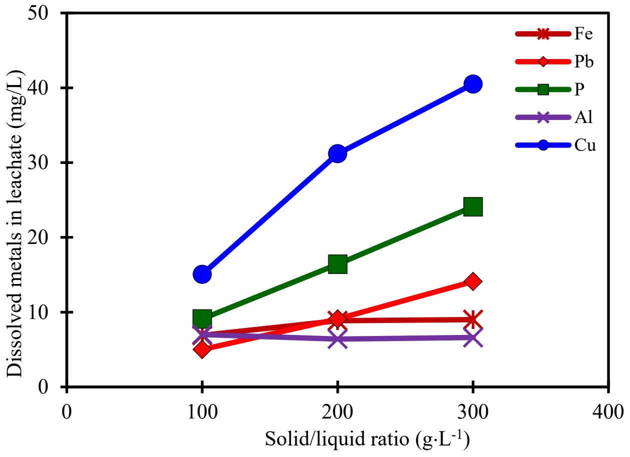


Figure 6. Effects of solid/liquid ratio on amount of dissolved metals in leachate (leaching condition: 2 M sulfuric concentration 2 M, 60 min leaching time).

3.3 Effects of leaching time on nickel leaching and amount of dissolved metals in leachate

Effects of leaching time on nickel leaching efficiency have been studied over the time period of 30 min to 180 min as shown in Figure 7. It was found that over the investigated leaching period, the nickel leaching efficiency reached an approximate range of 89% to 95%. It was also observed that over the leaching time period, the amount of certain impurities such as phosphorus, aluminium and lead stayed the same while that of iron increased slightly after leaching for 60 min as demonstrated in Figure 8.

For leaching step, dissolution of nickel precipitate of higher than 90% was achieved at the optimum leaching condition of 2 M sulfuric acid, solid to liquid ratio of 100:1 g·L^{-1} and leaching time of 60 min. The leachate obtained via the optimum leaching condition was further used as electrolyte in electrowinning experiment. However, before using as electrolyte the pH level of the leachate was adjusted to 2. The chemical composition of the electrolyte is shown in Table 2.

3.4 Nickel deposition via electrowinning

For the deposition of nickel via electrowinning process, and by varying electrical potential of 3.3, 3.5 and 3.7 V for 24 h, experimental result revealed that the electrical potential of 3.5 V applied in the middle range provided nickel deposit of highest purity of 99.14%, as graphically demonstrated in Figure 9. The uniformly dense with a smooth, bright and clean surface can be obtained from the optimal electrowinning test condition, as seen in Figure 10(a). For the nickel deposition, the nickel nuclei growing in each direction uniformly can be observed, as seen in Figure 10(b).

It can be explained that higher electrical potential could cause other metal ions to accumulate at the cathode while on the other hand, less electrical potential might result in better deposition of nickel ions but may take a longer time to extract nickel. Hence, electrowinning at the lowest electrical potential at 3.3 V gave the lowest recovery of nickel at 58.72% while electrowinning at 3.5 V again provided the highest nickel recovery at 61.66% with relatively greatest current efficiency of 15.48%. It can be seen that at low electrical potential, nickel recovery was less than that compared to a higher voltage because it might take a longer time to accumulate nickel ions at the cathode as previously mentioned. Using a high voltage however could increase the percentage of nickel recovery but contamination of impurity ions in the solution may result. By considering the current efficiency, rather low values were obtained in a range of only 10% to 16%. It means that the process required high energy for extraction. Future research work might be required to further define the electrowinning condition to optimize these parameters. Therefore, according to the varying electrical potentials used in this research, electrowinning at 3.5 V gave the optimum results of greatest nickel purity of 99.14%, recovery of 61.66% and current efficiency of 15.48%.

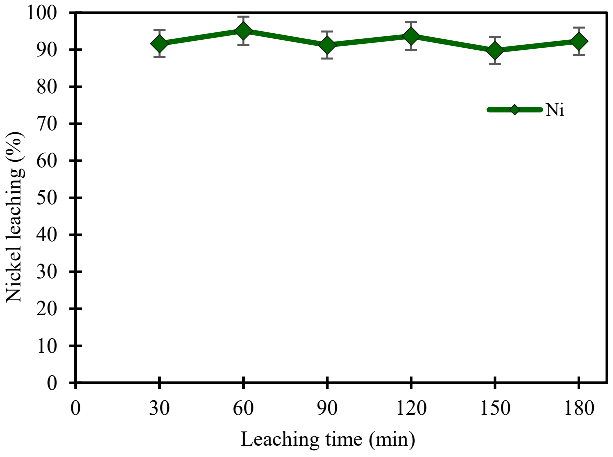


Figure 7. Effects of leaching time on nickel leaching (leaching condition: 2 M sulfuric acid concentration, 100:1 g·L^{-1} solid/liquid ratio).

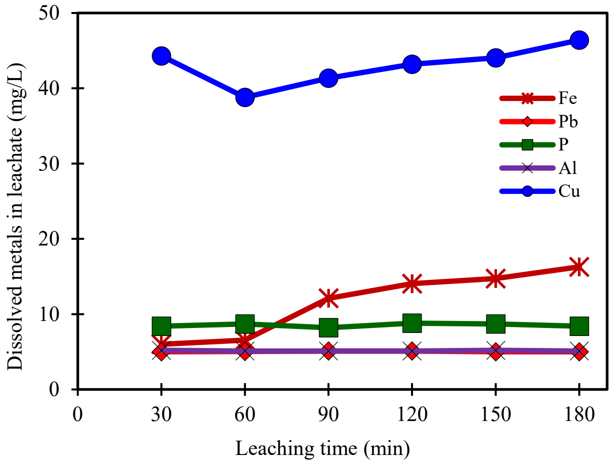


Figure 8. Effects of leaching time on amount of dissolved metals in leachate (leaching condition: 2 M sulfuric acid concentration, 100:1 g·L^{-1} solid/liquid ratio).

Table 2. Chemical analysis of electrowinning electrolyte by ICP-OES.

Element	Ni	Cu	Fe	Pb	P	Al
Concentration (mg·L^{-1})	155,300.0	14.2	2.4	8.2	n/a	n/a

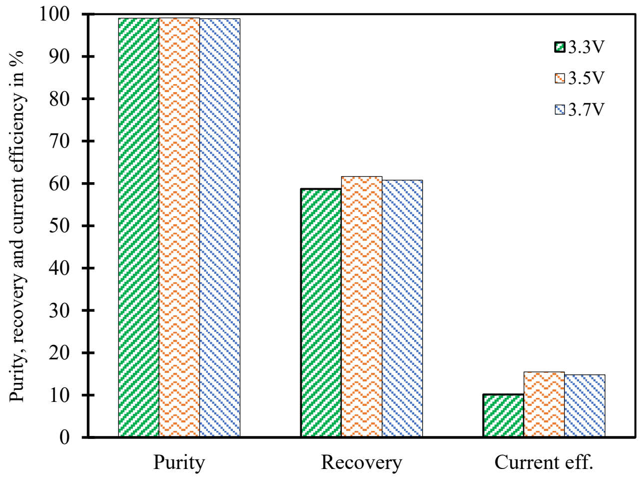
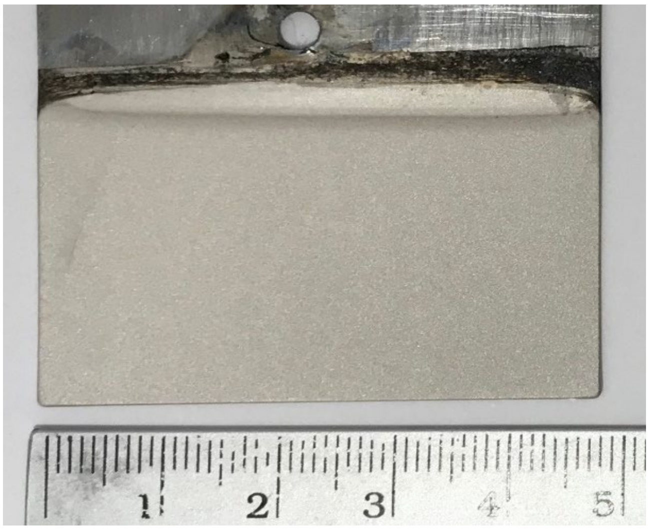
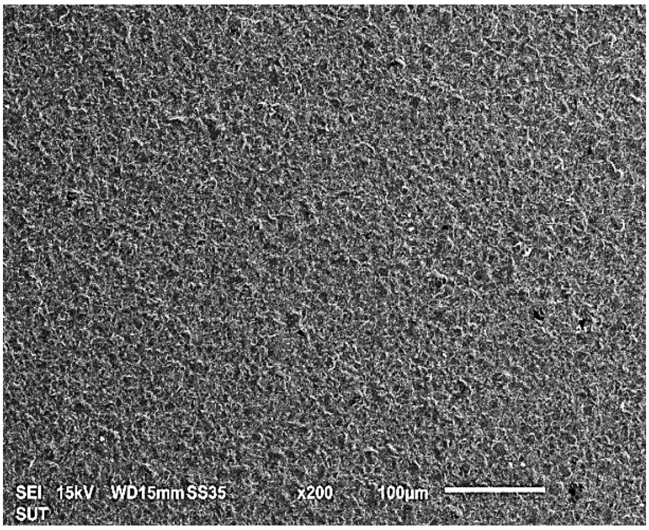


Figure 9. Purity, recovery of nickel deposited at cathode and current efficiency of electrowinning process at varied electrical potentials of 3.3 V to 3.7 V.



(a) Nickel deposition



(b) SEM image of nickel deposition

Figure 10. Ni deposition via electrowinning process (a) Photograph of nickel deposit (b) SEM image of nickel deposit cathode at 200x (electrowinning condition: 3.5 V cell voltage, 200 rpm stirring speed, ambient temperature).

4. Conclusions

According to experimental on recycling of spent electro nickel plating solution by hydrometallurgy and electrochemical methods, variables such as sulfuric acid concentration (1 M to 3 M), solid to liquid ratio (100 g·L^{-1} to 300 g·L^{-1}) and leaching time (30 min to 180 min) in the leaching step together with the electrical potential (3.3 V to 3.7 V) in the electrowinning step have been investigated to determine the optimum condition. The conclusions can be drawn as follows;

1. In the leaching step, increasing sulfuric acid concentration led to higher % leaching of nickel. The optimum sulfuric acid concentration was found to be at 2.0 M when considering the impurity level in the leachate after leaching.
2. The increase in solid to liquid ratio was found to reduce % leaching of nickel. The optimum solid to liquid ratio to for leaching of nickel precipitate was therefore at 100 g·L^{-1}, giving 91.96% leaching of nickel.
3. The leaching time of nickel precipitate over 30 min to 180 min gave % leaching of nickel in the range of 89% to 95%. The optimum period for leaching of nickel sludge was suggested to be 60 min, which can give the percentage of nickel leaching up to 95.14%.
4. The extraction of nickel metal using the electrical potential of 3.5 V gave the greatest purity of the nickel at 99.14%. Lower electrical potential at 3.3 V might require longer time for nickel deposited at the cathode while higher electrical potential at 3.7 V gave nickel of higher level of impurities. Via electrowinning process, nickel can be recovered from the spent electro nickel plating solutions of approximately 61%.

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References

[1] R. Idhayachander, and K. Palanivelu, "Electrolytic Recovery of Nickel from Spent Electroless Nickel Bath Solution," *E-Journal of Chemistry*, vol. 7, no. 4, pp. 1412-1420, 2010.

[2] D. A. Bertuol, F. D. R. Amado, H. Veit, J. Z. Ferreira, and A. M. Bernardes, "Recovery of Nickel and Cobalt from Spent NiMH Batteries by Electrowinning," *Chemical Engineering and Technology*, vol. 35, no. 12, pp. 2084-2092, 2012.

[3] K. Wang, L. Li, and T. Zhang, "Synthesis of Nickel Hydroxide and Its Electrochemical Performances," *International Journal of Electrochemical Science*, vol. 8, pp. 6252-6257, 2013.

[4] J. E. Silva, D. Soares, A. P. Paiva, J. A. Labrincha, and F. Castro, "Leaching behaviour of a galvanic sludge in sulphuric

acid and ammoniacal media," *Journal of Hazardous Materials*, vol. 121, no. 1-3, pp. 195-202, 2005.

[5] L. Li, N. Takahashi, K. Kaneko, T. Shimizu, and T. Takarada, "A novel method for nickel recovery and phosphorus removal from spent electroless nickel-plating solution," *Separation and Purification Technology*, vol. 147, pp. 237-244, 2015.

[6] N. Al-Mansi, and N. A. Monem, "Recovery of nickel oxide from spent catalyst," *Waste Management*, vol. 22, no. 1, pp. 85-90, 2002.

[7] V. Coman, B. Robotin, and P. Ilea, "Nickel recovery/removal from industrial wastes: A review," *Resources, Conservation and Recycling*, vol. 73, pp. 229-238, 2013.

[8] C. Lupi, M. Pasquali, and A. Dell'Era, "Studies concerning nickel electrowinning from acidic and alkaline electrolytes," *Minerals Engineering*, vol. 19, no. 12, pp. 1246-1250, 2006.

[9] J. E. Silva, D. Soares, A. P. Paiva, J. A. Labrincha, and F. Castro, "Solvent extraction applied to the recovery of heavy metals from galvanic sludge," *Journal of Hazardous Materials*, vol. 120, no. 1-3, pp. 113-118, 2005.

[10] Y. J. Lee, S. V. Rao, B. N. Kumar, D. J. Kang, and B. R. Reddy, "Nickel recovery from spent Raneynickel catalyst through dilute sulfuric acid leaching and soda ash precipitation," *Journal of Hazardous Materials*, vol. 176, no. 1-3, pp. 1122-1125, 2010.

[11] F. Veglio, R. Quaresima, P. Fornari, and S. Ubaldinib, "Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning," *Waste Management*, vol. 23, no. 3 pp. 245-252, 2003.

[12] N. M. Al-Mansi, and N. M. Abdel Monem, "Recovery of nickel oxide from spent catalyst," *Journal of Hazardous Materials*, vol. 22, no. 1, pp. 85-90, 2002.

[13] R. Wu, M. Oliazadeh, and A. Alfantazi, "Electrical conductivity and density of $NiSO_4/H_2SO_4$ solutions in the range of modern nickel electrorefining and electrowinning electrolytes," *Journal of Applied Electrochemistry*, vol. 33, no. 11, pp. 1043-1047, 2003.

[14] H. Y. Lee, "Separation and Recovery of Nickel from Spent Electroless Nickel-Plating Solutions with Hydrometallurgical Processes," *Separation and Purification Technology*, vol. 48, pp. 1602-1608, 2013.

[15] T. Benvenuti, R. S. Krapf, M. A. S. Rodrigues, A. M. Bernardes, and J. Zoppas-Ferreira, "Electrolytic Recovery of Nickel from Spent Electroless Nickel Bath Solution," *Separation and Purification Technology*, vol. 129, pp. 106-112, 2014.