Nickel extraction from nickel matte

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Abstract. In present work, the results of research activities to make nickel metal from nickel matte are presented. The research activities were covering **a**) nickel matte characterization using Inductively Couple plasma (ICP), Electron Probe Micro Analyzer (EPMA) and X-Ray Diffraction (XRD), **b**) nickel matte dissolution process to dissolve nickel from nickel matte into the spent electrolyte solutions that contains hydrochloric acid, **c**) purification of nickel chloride leach solution by copper cementation process to remove copper using nickel matte, selective precipitation process to remove iron, solvent extraction using Tri normal octyl amine to separate cobalt from nickel chloride solutions and **d**) Nickel electro winning process to precipitate nickel into the cathode surface from purified nickel chloride solution by using direct current. The research activities created 99, 72 % pure nickel metal as the final product of the process.

1. Introduction
Nickel is an important metal for making stainless steel, high temperature steel, magnetic materials, nickel plating, non ferrous alloys, catalyst, fuel cell and chemicals. Cause of wider application of nickel at Industries, the world nickel production tends to increase. In 2013, the world nickel production increased 10 times compared with the world nickel production in 1950 [1]. The increased of world nickel consumption was stimulated by a new discoveries of variety nickel alloys for industrial application and development of new materials [2, 3].

In line with the progress of Indonesian industries, the nickel demand increases, mostly of nickel are used as raw materials for electroplating industries in Indonesia. However in future, in line with the progress of Indonesian industries, the nickel demand is estimated will increase. Nowadays to full fill nickel demand in Indonesia, nickel have to be imported from foreign countries because there are not industry that can produce pure nickel metals from the available raw material in Indonesia. Referring to the data from the ministry of Industry of the republic of Indonesia, the value of imported nickel to Indonesia is 36 million US $ at 2016 [4]. The high imported nickel product to Indonesia creates an opportunity to make nickel metal from the available nickel resources in Indonesia. There are nickel laterite ores that can be used for nickel making and spreads at several areas in Indonesia such as at South Sulawesi, Maluku and Papua that can be used as raw material for nickel making [5,6]. Some of those nickel laterite ores has already been utilized by P.T Aneka Tambang to make Ferro nickel (25 % nickel and 75 % iron) and by P.T Vale to make nickel matte (73 % nickel and 20 % sulfur), however industry that can produce pure nickel metals has not available yet in Indonesia. Therefore to obtain the prospective process for nickel making from the available nickel resources in Indonesian, the Research

centre for metallurgy and material LIPI conducted several laboratory tests to make pure nickel metal from nickel matte. The results of those laboratory tests are presented in this paper.

2. Characteristic of nickel matte

Nickel matte characterizations process was carried out by using Inductively Couple Plasma (ICP), Electron Probe Micro Analyzer (EPMA) and X-Ray Diffraction (XRD) that has already been reported in our paper [7]. The result of nickel matte analysis using ICP at Table 1 shows that nickel and sulfur becomes the main elements in nickel matte. Another element such as cobalt, iron, copper, arsenic and lead exist as minor elements. The result of microanalysis study using EPMA shows that nickel, sulfur and other elements that available at nickel matte forms a complex compound formation, while result of analysis by using XRD shows that Ni_2S_3 exists as a main phase in nickel matte.

Table 1. The chemical composition of nickel matte [7]

Elements	Ni	Co	Fe	Cu	As	Pb	S
%	73	0.8	0.6	3	0.2	0.003	20

3. Process Flow sheet for nickel making from nickel matte

Result of nickel matte characterization using ICP, EPMA and XRD shows that Ni_2S_3 is the main phase in nickel matte, another elements such as cobalt, iron, arsenic, copper and lead are existing as minor elements that forms a complex compound formation, and therefore a process alternative to separate nickel from another elements in nickel matte are through nickel matte electro refining [8], or through a combination processes of hydro and electrometallurgy as shown in process flow sheet at Figure 1.
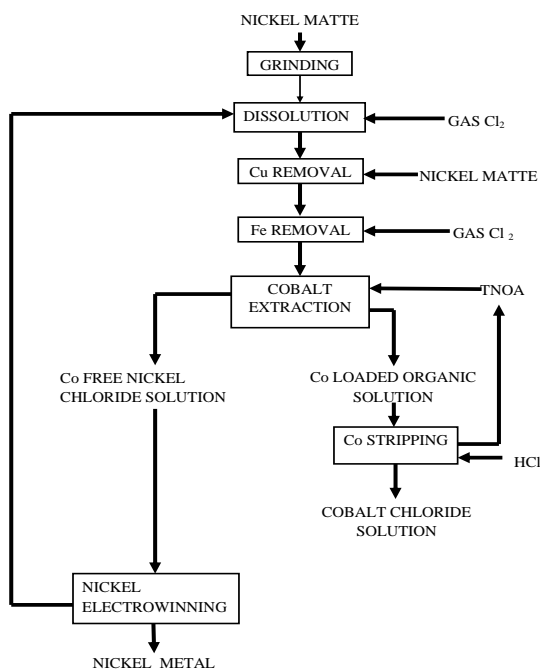

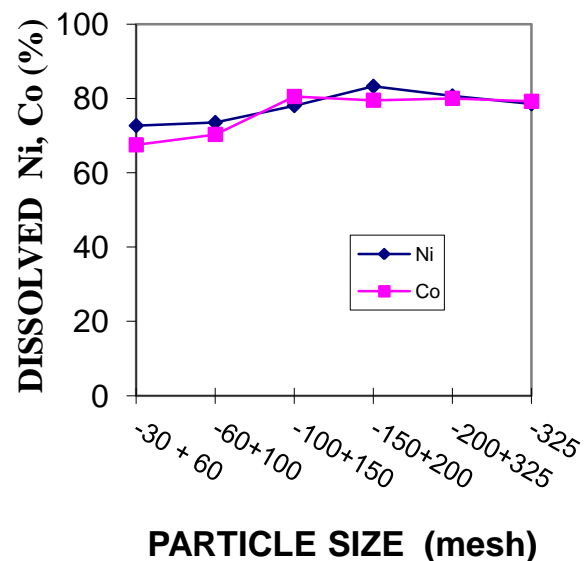**Figure 1.** Process flow sheet for nickel making

Figure 2. Effect of particle size on dissolution Ni and Co [9]

The process flow sheet at Figure 1 consists of several steps of process i.e. grinding process, nickel matte dissolution process to dissolve nickel from nickel matte into spent electrolyte solutions that contains hydro chloride acid from electro winning process, purification process to remove, copper, iron and cobalt from leached nickel chloride solution. In this purification process, copper are removed from the leach solutions by cementation process using nickel matte, iron are removed from leach solutions by selective precipitation process using chlorine gas and cobalt are separated from nickel chloride leach solutions by solvent extraction process. The final process is nickel electro winning. At this process nickel is deposited from purified nickel chloride solutions at the surface of cathode by using direct current.

4. Grinding process

Nickel matte particle size plays an important role in nickel dissolution process from nickel matte into the acid solutions. The more finer particle size are generally gives better result to the dissolution process because the smaller particle has larger surface area that creates good contact between nickel matte particle with the acid leach solution, and therefore it will stimulate and accelerated the nickel and cobalt dissolution process from nickel matte into acid solutions.

An experiment to investigate effect of nickel matte particle size on nickel and cobalt dissolution from nickel matte in to hydrochloric acid solutions has been investigated by author. At that experiment, the nickel matte particle size were varied from – 30 mesh up to -325 mesh, and dissolution experiment were carried out using 16 % volume aqueous hydrochloric acid solution at temperature 95°C, with chlorine gas flow rate 100 ml/minute, for dissolution time 1 hours. The result at Figure 2 shows that the finer nickel matte particle size increased the nickel and cobalt dissolution from nickel matte. For ground nickel matte that has particle size - 60 mesh, only 73% of nickel and 68 % of cobalt were dissolved from nickel matte. However if the nickel matte particle size was ground up to -100 mesh, the dissolved nickel and cobalt increased respectively to 78 % for nickel and 80 % for cobalt [9].

5. Nickel matte dissolution process into spent electrolyte contains hydrochloric acid solutions

The simplified nickel matte dissolution reaction in hydrochloric acid solution under chlorine gas addition is taking place according to the following reactions:

$$Ni_3S_2 \quad + \quad Cl_2 \quad \rightarrow \quad 3\,Ni^{2+} \quad + \quad 2\,S^o \quad\quad + \quad 2\,Cl^- \qquad\qquad (1)$$
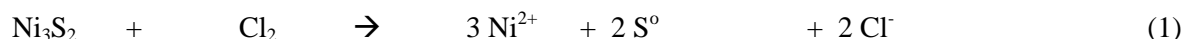
That dissolution reaction is affected by dissolution temperature, hydrochloric acid concentration in leach solutions, copper and chlorine gas addition into the leach solution [7]. The effect of temperature on nickel and cobalt dissolution from nickel matte into the 16 % volume hydrochloric acid solutions at temperature from 50 ^{o} C to 95 ^{o} C, and chlorine gas flow rate 60 ml/minute for 90 minute dissolution time at Figure 3 shows that the increase of dissolution temperature from 50 ^{o} C to 80 ^{o} C did not give any significant effect to the dissolution of nickel and cobalt from nickel matte. However if the dissolution temperature were increased from 80 ^{o} C to 95 ^{o} C, the dissolved nickel and cobalt were respectively increased to 100 % for nickel and 98 % for cobalt.

The effect of hydrochloric acid concentration on nickel dissolution has also been observed using spent electrolyte as leach solutions and the concentration of hydrochloric acid in spent electrolyte were varied from 1 % up to 16 % volume. The result of experiment at Figure 4 shows that the increase of hydrochloric acid concentration in spent electrolyte solutions from 1 % to 16 % increased the dissolved nickel from 25 % to 90 % and dissolved cobalt from 48 % to 100 % [7].

Copper in leach solutions influences the nickel dissolution process. Copper gives a catalytic effect to the nickel dissolution process. Our result of experiment at Figure 5 shows that the increase of $CuCl_2$ concentration from 0 gram/liter to 40 gram/liter in the leach solutions lead to increase the dissolved nickel from 61 % to 90 % and dissolved cobalt from 77 % to 93 % [7]. The same result of copper catalytic effect during nickel dissolution process was also reported by Wladyslawa Mulak [10].

The catalytic effect of copper during nickel matte dissolution process is taking place according to the following reactions:
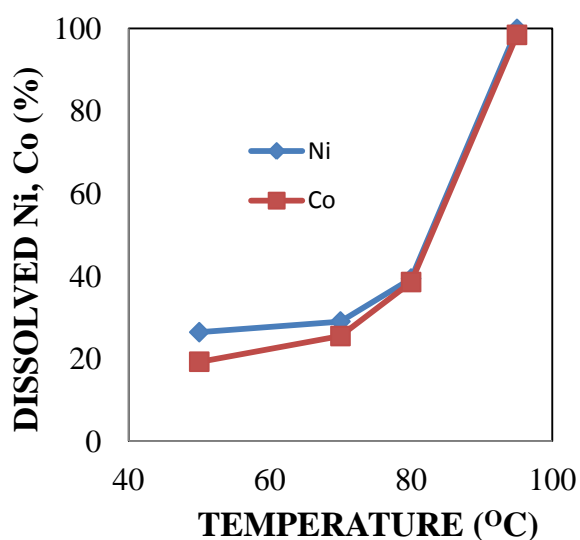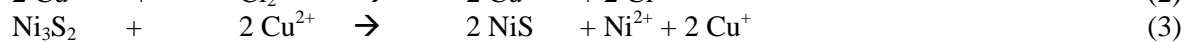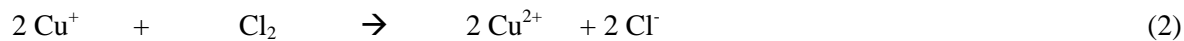
$$2\,Cu^+ \quad + \quad Cl_2 \quad \rightarrow \quad 2\,Cu^{2+} \quad + 2\,Cl^- \tag{2}$$

$$Ni_3S_2 \quad + \quad 2\,Cu^{2+} \quad \rightarrow \quad 2\,NiS \quad + Ni^{2+} + 2\,Cu^+ \tag{3}$$

$$NiS \quad + \quad 2\,Cu^{2+} \quad \rightarrow \quad Ni^{2+} \quad + 2\,Cu^+ + S^o \tag{4}$$

$$Cu_2S \quad + \quad S^o \quad \rightarrow \quad 2\,CuS \tag{5}$$

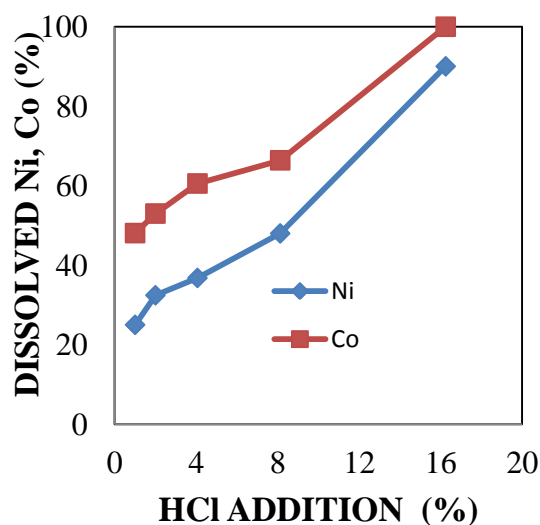**Figure 3.** Effect of Temperature on dissolution Ni and Co

Figure 4. Effect of HCl addition on dissolution Ni and Co
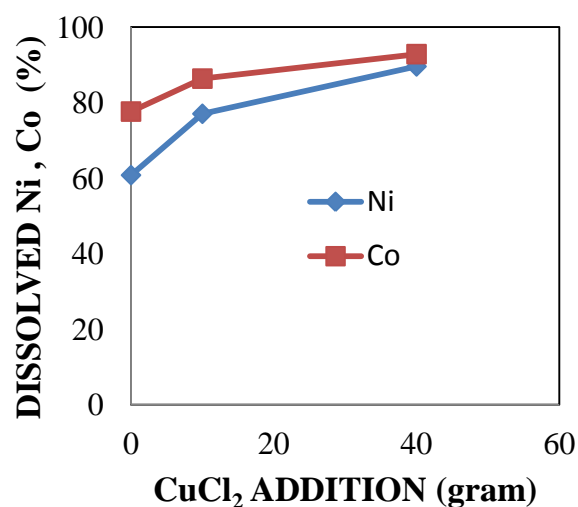

Figure 5. Effect of CuCl$_2$ addition on dissolution Ni and Co [7]
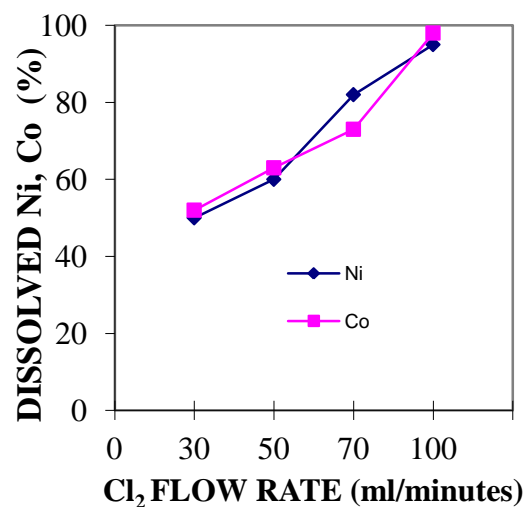

Figure 6. Effect of Cl$_2$ addition on dissolution Ni and Co [7]

In case of chlorine gas effect on nickel dissolution process, our result of experiment at Figure 6 shows that during nickel matte dissolution into 16 % volume hydrochloric solution at temperature 95 $^{\circ}$ C, the increase of chlorine gas flow rate from 30 ml/minute to 100 ml/minute lead to increase the dissolved nickel from 50 %, to 95 %, and dissolved Cobalt from 52 % to 98 % [7].

6. Copper removal from nickel chloride leached solutions

The produced nickel chloride leached solutions from the nickel matte dissolution process were containing impurities elements such as Cu 0.15 gram/liter, Fe 0.33 gram/liter and cobalt 0.013 gram/liter. Those impurities elements have to be removed from the nickel chloride solutions because it will influence purity of the final product nickel metal. There are many alternative process to remove ionic copper from the solutions such as by precipitation of ionic copper using activated sulfur powder [11], copper cementation using Aluminum canning sheet [12], copper cementation using nickel plate steel [13], the cementation of copper from copper sulfate on zinc using organic compound sodium diethyldithiocarbamate as additive [14], copper cementation from copper sulfate solutions using iron powder [15], copper cementation from spent copper-pickle sulfate solution by zinc ash [16], and copper removal from the nickel chloride solutions using nickel matte that was investigated by author [17]. Comparing of those copper removing processes, the copper cementation using nickel matte is most prospective ways to remove ionic copper from solutions because nickel matte is raw materials for nickel making process, and the successfully of this latest process is affected by the quantities of nickel matte added, temperature and copper precipitation time. Result of our experiment to remove ionic copper from nickel chloride solutions that contains copper 0.15 gram/liter at temperature 75 o C and cementation time 60 minutes, at Figure 7 shows that the increase of nickel matte addition from 0.14 gram to 0.84 gram lead to increase the percentage of precipitated copper from 28 % to 94 %, and when the cementation temperature were increased from 30 0 C to 90 o C, the result at Figure 8 shows that the cemented copper increased, almost 100 % of ionic copper can be cemented from nickel chloride solutions at temperature 90 0 C using nickel matte [17].
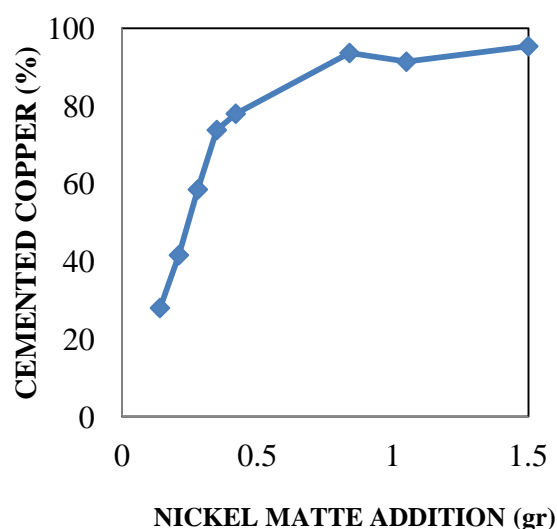

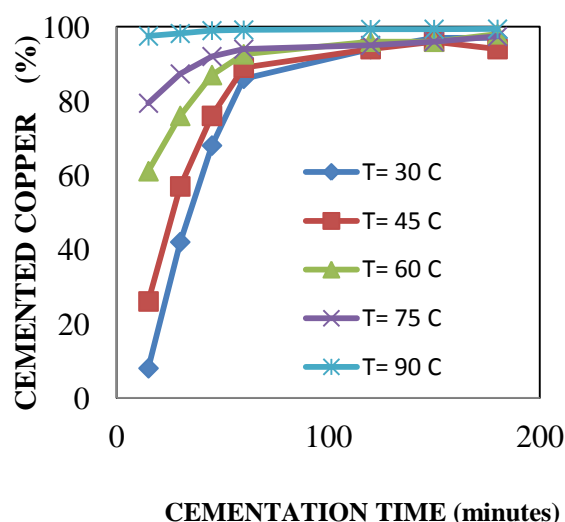**Figure 7**. Effect of nickel matte addition on cemented copper

Figure 8. Effect of temperature on cemented copper

7. Iron removal from nickel chloride leached solutions

Nickel chloride leached solution produced from nickel matte dissolution process contains 0.33 gram/liter iron. That ionic iron should be removed from nickel chloride leached solutions because it influences the purity of the final product nickel metal. There are many alternative process to remove ionic iron from the leach solutions such as by using solvent extraction [18], oxidation of ionic iron available in the solution using dissolved oxygen [19], oxidation using mixed SO_2 and oxygen [20], iron removal with the iron phosphate precipitation process [21], magnetic precipitation from nickel rich solution by slow oxidation at pH 2.0-2.2 at temperature 90 -100° C [22], and in our experiment, iron was removed from nickel chloride solutions by oxidation of ionic Ferro to ionic ferric in the solution using chlorine gas, and controlling the solution potential & pH to precipitate ionic ferric from the solutions[23]. Among those methods, the iron removal by using chlorine gas and pH controlling to precipitate iron from the solutions is the most potential ways to make a purest nickel metal. This method is influenced by temperature and solutions pH. Our results of iron precipitation experiments at Figure 9 and Figure 10 show that the precipitated iron at solution pH = 3.25 increased if the precipitation temperature were increased from 40° C to 50° C. The increased of the precipitated iron with the temperature increase is caused by kinetic and thermodynamic aspect of the precipitation reactions. From kinetic aspect, the rate of precipitation will increase if the solution temperatures are increased and from thermodynamic aspect the increase of solution temperature shift the equilibrium curve of iron with its oxide to the left side and therefore at higher temperature iron will easily be precipitated [24]. Another experimental result at Figure 10 shows that for temperature 50° C and precipitation time 60 minutes, the precipitated iron increased from 85 % to 100 %. if the solution pH were increased from pH 2 to pH 3.25.
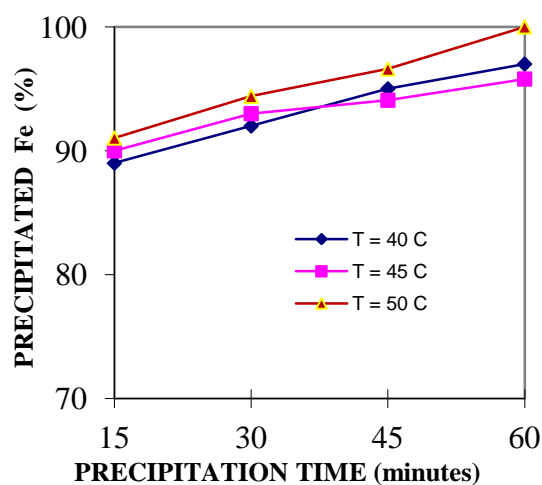

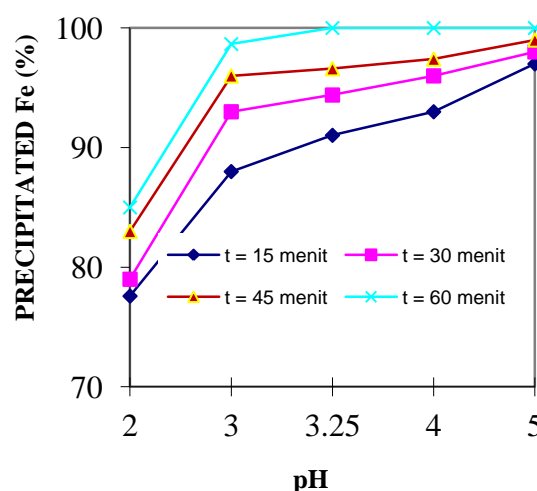**Figure 9.** Effect of temperature on precipitation Fe

Figure 10. Effect of solution pH on precipitation Fe [23]

8. Cobalt Separation from nickel chloride solutions by solvent extraction

Cobalt separation from nickel chloride leached solutions is a final step in purification of nickel chloride leached solutions. There are many alternative processes to separate cobalt from the aqueous solution such as by selective precipitation and solvent extraction [25]. The separation of cobalt from nickel by solvent extraction will depend on the characteristic of their mother solutions [26]. Therefore, there are many commercial organic materials to separate cobalt from nickel by solvent extraction. The choice of those organic materials for solvent extraction process is depending on the characteristic of aqueous solution in which cobalt and nickel exist together in the solutions. Amine

compound with varieties trade name are generally used to separate cobalt from nickel chloride solutions. Those amine compound are *Alamine® 336, Alamine® 308, and Adogen® 381,* while for the aqueous sulfate solutions, versatic 10, D2EHPA (di(2-etylheksyl) phosphoric acid, organo phosphoric acid with trade name PC-88, and Cyanex 272 are generally used to separate cobalt by solvent extraction. In ammoniac solution *ketoximes* with trade name *LIX® 87QN, LIX® 8* are generally used to separate cobalt. Although there were organic solvent for solvent extraction process to separate nickel and cobalt, there are still problems in application of those solvent, and therefore Cheng conducted research to separate nickel and cobalt containing in the solution from nickel laterite processing which contains Mn, Mg and Ca. Their research result shows that mixed organic compound containing Versatic 10, LIX 63 and Tri butyl phosphate can be used to separate nickel and cobalt from solutions that containing Mn, Mg and Ca [27, 28], and mixed organic solution Versatic 10 and Acorga CLX 50 can be used to recover nickel and cobalt from leach solutions of nickel laterites by solvent extraction [29]. Those result of solvent extraction experiments need additional study to separate cobalt from nickel containing solutions. In our study to separate cobalt from nickel chloride leach solutions, the solvent extraction process were choose using organic compound Tri Normal octyl Amine (TNOA) as solvent and Shell soll AB as diluents [30]. The result of our solvent extraction experiment at Figure 11 shows that cobalt extraction slightly decreased if the solution pH were increased from pH 3 to pH 4, that is caused by characteristic of octyl amine that generally more active to extract cobalt at lower solution pH [31]. Result of our experiment shows that almost 98 % of cobalt can be extracted from nickel chloride solutions by TNOA at aqueous to organic phase (A/O) ratio = 1, room temperature, solution pH = 3 and extraction time 30 minutes [30]. The cobalt extraction by TNOA is effected by interaction between cobalt with chloride ion in solutions as shown at Figure 12. In aqueous phase ionic cobalt reacts with chloric ions to forms a chloro complex compound ($CoCl_4^{2-}$). This compound then move from aqueous phase to interface phase. At same time TNOA that have already reacted with chloride ions ($R_3NH^+Cl^-$) move from organic phase to interface phase and react with ($CoCl_4^{2-}$) to form ($R_3NH^+)_2CoCl_4^{2-}$ and chloride ion Cl^-. The phase ($R_3NH^+)_2CoCl_4^{2-}$ then goes to organic phase and chloride ion goes to aqueous phase [32]. The data at Figure 11 shows that cobalt extraction increases if A/O ratio decreases. At lower A/O, the TNOA concentration is high that lead to increase the cobalt extraction. However, if the A/O ratio increases, the TNOA concentration decreases and cobalt extraction decreases.
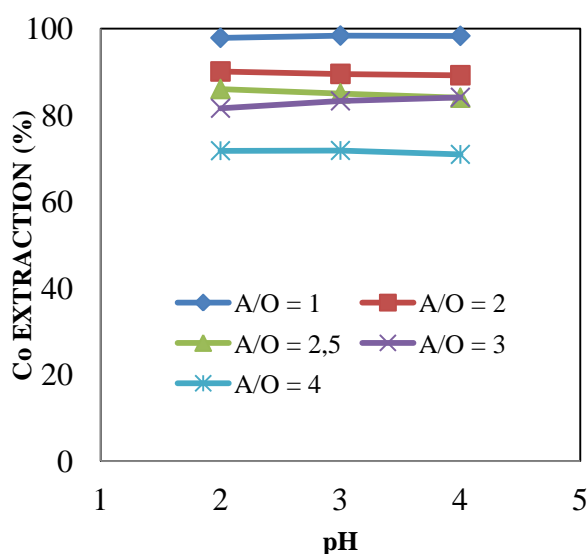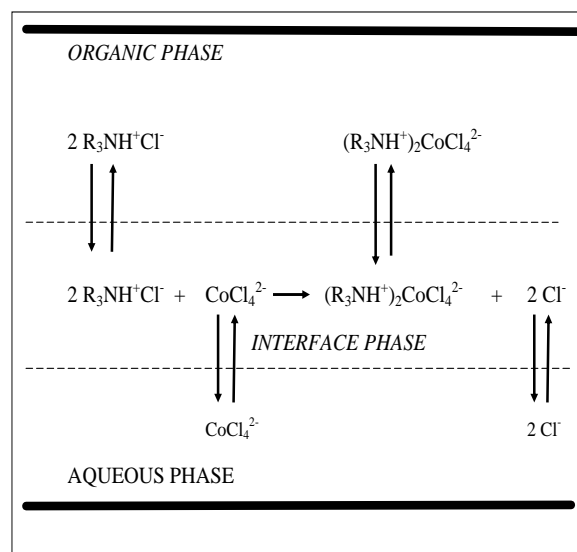

Figure 11. Effect of pH on cobalt extraction [30]

Figure 12. Some equilibrium involved in the extraction of cobalt from a chloride system using

tertiary amine [32]

9. Nickel electro winning process

The schematic apparatus for nickel electro winning process is presented at Figure 13. The electro winning cell consists of a bath that is containing of nickel chloride electrolyte solutions, positive electrode and negative electrode. The negative electrode (cathode) was made from titanium plate and the positive electrode (Anode) was made from Ruthenium oxide coated titanium plate material. The main reaction for nickel electro winning process in chloride solution takes place according to the equations 6 until 9. Nickel is deposited at the surface of cathode and hydrogen gas is generated according to the following reactions:

$$Ni^{2+} \quad + \quad 2e^- \quad\rightarrow\quad Ni^o \tag{6}$$
$$2H^+ \quad + \quad 2e- \quad\rightarrow\quad H_2 \tag{7}$$

At anode, chlorine gas and oxygen gas will be generated according to the following equation:

$$2Cl^- \quad\rightarrow\quad Cl_2 \quad + \quad 2e \tag{8}$$
$$H_2O \quad\rightarrow\quad 2H^+ \quad + \quad \tfrac{1}{2}\,O_2 + \quad 2\,e- \tag{9}$$
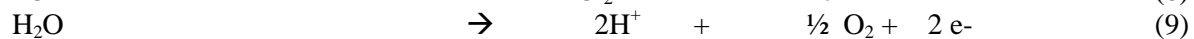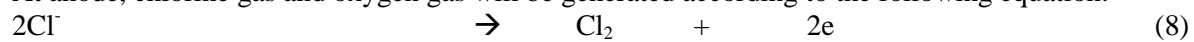
The chlorine, oxygen and hydrogen gases are produced by side reaction of nickel electro winning process, they consumes energy and reduced the current efficiency of nickel deposition process at cathode. The nickel current efficiency is ratio of actual nickel deposited at cathode with theoretical weight of nickel deposited at cathode that is calculated by equations 10.

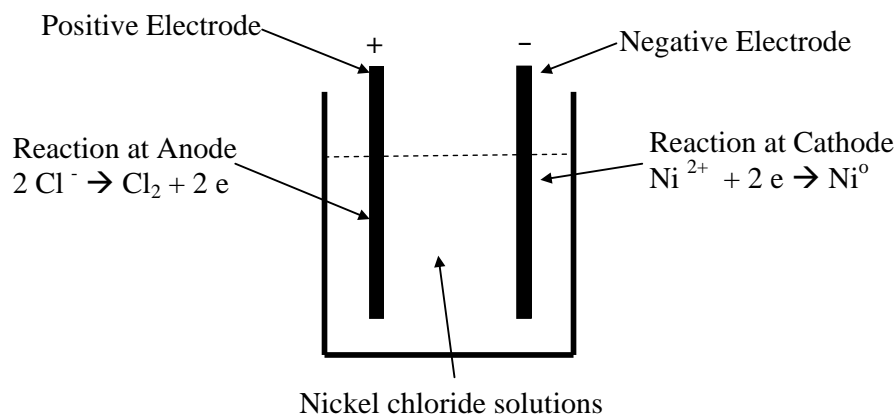$$\text{Current efficiency} = \frac{W_A}{W_T} \times 100\% \tag{10}$$

Figure 13. Nickel electro winning apparatus

Theoretical weight of nickel deposited at cathode (W_T) was calculated by Faraday law [33] according to equation 11.

$$W_T \quad = \quad i\,e_{Ni}\,t \tag{11}$$

Whereas:

W_A = weight of deposited nickel at cathode
W_T = theoretical weight of nickel deposited at cathode calculated by Faraday law
i = Current (Ampere)

e_{Ni} = equivalent weight for nickel
t   = deposition time (second)

The result of our nickel electro winning experiment using nickel chloride electrolyte solutions contains 55 gram/liter nickel, at current density 2 Ampere per square decimeter (ASD), at temperature $50^{o}C$ and solution pH = 1 show that almost 97 % of current efficiency was obtained and the final nickel metal deposited at cathode side has chemical composition as shows at Table 2.

Table 2. The chemical analysis of nickel deposited at cathode.

Element	Ni	Co	Zn	Cu	Fe
%	99,72	0,16	0,04	0,04	0,04

10. Conclusions

- Nickel metal with purity 99, 72 % can be made from nickel matte by using Hydro and electrometallurgy processes that consist of a) nickel matte dissolution process using spent electrolyte that containing hydrochloric acid solutions to dissolve nickel and cobalt from nickel matte, b) solution purification to remove copper, iron and cobalt from nickel chloride leached solutions and c) nickel electro winning process to deposited nickel from nickel chloride solutions.
- At dissolution process, almost 90 % of nickel and 100 % of cobalt were dissolved from nickel mate into the spent electrolyte that containing 16 % volume aqueous hydrochloric acid solutions at temperature 95° C and dissolution time 180 minutes.
- At purification process, Almost 100 % of ionic copper can be removed from the nickel chloride solutions by cementation using nickel matte at temperature 90^{0} C and almost 100 % of iron was removed from the nickel chloride solution by chlorine gas addition at temperature 50° C and solution pH 3,25. For Cobalt removal from nickel chloride solutions, the solvent extraction process to separate cobalt from nickel chloride using Tri normal octyl amine able to extract 100 % of cobalt into TNOA solutions at A/O (Aqueous to organic) ratio 1 and solution pH 3.
- The nickel electro winning process to deposit nickel from nickel chloride solutions that containing 55 gram/liter nickel, at current density 2 Ampere per square decimeter (ASD), temperature 50° C and pH = 1 created current efficiency 97 % and nickel metal with purity 99,72 %.

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