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INFLUENCE OF ELECTROLYTE MOLARITY AND APPLIED VOLTAGE ON THE PURIFICATION OF FERRONICKEL BY ELECTROLYSIS METHOD

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Abstract

The current advancements in the automotive industry highlight the critical need for electric vehicles, which require a reliable supply of nickel for battery production. A potential nickel source is Ferronickel's local content, which can be used as a secondary resource. However, research on converting smelted Ferronickel into electrolytic nickel is still limited. This study aims to examine the effects of electrolyte molarity and applied voltage during the electrolysis process for refining Ferronickel. The molarities of HCl employed in this research are 0.1, 0.25, 0.5, 0.75, and 1 M for 2 hours. Additionally, the molarities of HCl are set at 2, 3, and 4 M for 6 hours. Further experiments were performed using varying voltages of 1, 2, 4, 6, and 8 V while keeping the solution concentration constant at 1 M and maintaining an electrolysis duration of 2 hours. The electrolysis solution was subsequently analyzed using the AAS (atomic absorption spectrophotometry) test. The results indicated that higher molarity levels were associated with increased current, resulting in faster reaction rates and greater solubilization of nickel metal. The Ni concentration rose with higher molarity, increasing from 76.50 mg/L in .25 M HCl to 91.88 mg/L in 1 M HCl. In contrast, the Fe concentration remained nearly constant across various molarity levels, ranging from 11.81 mg/L in .25 M HCl to 11.95 mg/L in 1 M HCl, suggesting a minimal influence of molarity below 1 M. Fe exhibited a strong positive correlation with increasing electrolyte molarity, showing a significant rise in concentration from 49.06 g/L at 2 M to 90.17 g/L at 4 M. Ni showed a more modest response to elevated molarity, with concentrations increasing from 11.95 g/L at 2 M to 22.70 g/L at 4 M. The Ni concentration increased with the applied voltage up to 6 V, reaching 95.57 mg/L, but then decreased to 77.67 mg/L at 8 V, indicating that the optimum voltage is 6 V. The Fe concentration displayed slight fluctuations but remained relatively stable across different voltage levels, measuring 11.81 mg/L at 1 V and 12.28 mg/L at 8 V, indicating that the applied voltage does not significantly influence Fe concentration in the solution.

Keywords: *Ferronickel, electrolysis, molarity, applied voltage, concentration*

1. INTRODUCTION

A substantial supply of nickel is required as a battery raw material to support the government's domestic electric vehicle production initiative. One potential source of nickel is local-content ferronickel (FeNi), which can be utilized as a secondary resource. However, FeNi applications are currently limited. It is primarily used as a raw material for stainless steel production. To date, ferronickel has not been effectively utilized for other purposes [1]-[4].

According to United States Patent No. 3,755,113 [4] and findings published by Moussoulos [5], the production process of electrolytic nickel from ferronickel

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demonstrates that ferronickel products with a nickel content of 80-85% can be purified to 99.95% Ni through the electrorefining method. This process can significantly expand the market potential of ferronickel, which is currently predominantly utilized in stainless steel manufacturing. However, there are limitations, including the requirement that a Feni anode with a minimum Ni content of 80% be used to obtain high nickel with high purity by electrorefining.

Feni extracted from Ni laterite ore with a pyrometallurgical process has a Ni content of around ± 20%. So, in both studies, the anode from Feni was not used; it made its anode material with a composition of Ni above 80%. Therefore, a precise method is needed to convert Feni into Ni electrolytic with the available Feni Anode.

Several studies have been conducted [6–9] to separate Ni from other metals. Chen et al.[6] Crushed and calcined the battery and dissolved it with acetic acid and water. Ni and Cd dissolve as $Ni(CHCOO)$ and $Cd(CHCOO)$, while $Fe(CHCOO)OH$ is insoluble in water. So, that method can be used to separate Ni and Fe.

The ferronickel refining process using the electrolysis method uses an electrolyte solution as a conductor medium to conduct electric current between the anode and the cathode. The electrolyte solution can also be a catalyst to accelerate the reaction rate. The molarity of the electrolyte solution used can affect the process that occurs in electrolysis and the quality of the results obtained.

This study utilized HCl (hydrochloric acid) as the electrolyte solution. HCl was chosen due to its strong acid properties, which allow complete ionization in solution. This characteristic makes HCl an effective catalyst within the electrolyte solution, facilitating a rapid reaction rate through enhanced ionic conductivity and efficient electrochemical kinetics [10].

This study focuses on the influence of electrolyte molarity and applied voltage in the electrolysis process for refining ferronickel (FeNi). The electrolyte solution's concentration and applied voltage can significantly impact electrolysis. Thus, when employing electrolysis methods in ferronickel refining, it is crucial to consider the effects of electrolyte molarity and applied voltage to achieve optimal refining results.

2. MATERIALS AND METHODS

2.1 Sample and Electrolyte Preparation

This research aims to obtain secondary nickel (Ni) and cobalt (Co) resources through the electrorefining of ferronickel shot. Ferronickel shot from PT Antam Tbk. is available in two composition variations: LCS (low carbon shot) and HCS (high carbon shot). Based on XRF (x-ray fluorescence) analysis, the composition of the HCS samples is in Table 1.

Tabel 1. Composition of ferronickel shot

Element	Composition (wt.%)
Fe	77.369
C	1.140
Ni	18.490
Co	0.340
Mn	0.040
Cr	0.890
Si	0.430
P	0.017
S	1.275
Cu	0.009

Ferronickel was cast into blocks with 11 x 1 x 0.5 cm dimensions to use as the anode in the electrolysis process (Fig. 1). The cast ferronickel samples were cut into pieces according to predetermined dimensions. Subsequently, the samples were cleaned of impurities using a grinding machine and weighed to determine their mass before the electrolysis reaction.

Figure 1. Ferronickel anode

Electrodes serve as conductive media that allow electric current to flow from one medium to another. Typically made from metals like copper, silver, tin, or zinc, electrodes can also be composed of non-metallic conductive materials like graphite[11]. In this study, graphite was used as the cathode, while the ferronickel block was used as the anode. The cathode uses graphite (C) as a cylinder with a length of 11 cm and a diameter of 1 cm.

The electrolyte solution was prepared by diluting 37% HCl in distilled water. HCl, a strong acid commonly used in industry, is an effective electrolyte in solution [12]. The molarities of HCl used in this research are 0.1, 0.25, 0.5, 0.75, and 1 M.

2.2 Electrolysis Process

Various concentrations of HCl were employed to investigate the influence of electrolyte molarity on the electrolysis process. The electrolysis was conducted in a 250 ml glass beaker containing 200 ml of the prepared electrolyte solution. A ferronickel block served as the anode, while graphite was used as the cathode, both immersed in the electrolyte. The HCl molarities studied were 0.1, 0.25, 0.5, 0.75, and 1 M. The anode and cathode were connected to the positive and negative terminals of a Dekko PS-3030Q rectifier, respectively, with an applied voltage of 1 V. The electrolysis was carried out for 2 hours. Additional experiments were conducted using higher HCl molarities of 2, 3, and 4 M, with an applied voltage of 2 V and an extended electrolysis duration of 6 hours.

Subsequent experiments were performed at varying voltages of 1, 2, 4, 6, and 8 V to elucidate the effect of applied voltage on electrolysis while maintaining a constant HCl concentration of 1 M and an electrolysis duration of 2 hours.

2.3 Quantitative Determination of Chemical Element

AAS (atomic absorption spectrophotometry) is a chemical analysis instrument that uses the principle of energy absorbed by atoms to analyze the concentration of analytes in a sample. By absorbing energy, electrons in the atom are quickly excited to a higher orbital [13].

The parameters varied in this research include the concentration of the HCl electrolyte solution, precisely 0.1, 0.25, 0.5, 0.75, and 1 M, and the applied voltage that is 1, 2, 4, 6, and 8V. After electrolysis, the solution was filtered using filter paper to separate it from impurities. The filtered solution was then transferred to a 100 ml bottle for analysis using AAS to determine its elemental composition.

For the experiments conducted with higher HCl molarities of 2, 3, and 4 M under an applied voltage of 2 V and an electrolysis duration of 6 hours, the electrolyte was characterized using a 725 ICP-OES (inductively coupled plasma optical emission spectroscopy) instrument.

3 RESULT AND DISCUSSION

3.1 The Effect of Electrolyte Molarity

The electrolysis results for each sample varied according to the concentration levels used. The electrolyte solutions are depicted in Fig. 2. Observations indicate that higher molarity levels correspond to increased current. Consequently, the electric current in each sample varied with the molarity concentration, leading to a faster reaction rate and increased solubilization of nickel metal.

Figure 2. Electrolysis solution

Based on the standard reduction potential at 25 ^{o}C, the Ni reaction in Equation 1 and for Fe oxidation reaction in Equation 2 [14].

$Ni^{+} + 2e^{-} \rightarrow Ni$ $E^{o} = -0.250$ V (1)
$Fe^{++} + 2e^{-} \rightarrow Fe$ $E^{o} = -0.440$ V (2)

The relationship between the standard reduction potentials of Ni and Fe and the rate of electrolysis at an anode composed of Fe and Ni with a graphite cathode is governed by the relative tendencies of these metals to undergo oxidation. Iron, having a more negative standard reduction potential (-0.44 V) compared to nickel (-0.25 V), is more susceptible to oxidation. Consequently, during the electrolytic process, the oxidation of iron at the anode typically proceeds faster than that of nickel under equivalent conditions.

Figure 3 shows dissolved Ni and Fe resulting from electrolysis at a 1 V voltage measured using AAS based on differences in electrolyte molarity. Fe concentration remains almost constant across different molarity levels, with only slight fluctuations. In 0.25 M HCl, it is 11.81 mg/l, and in 1 M HCl, it is 11.95 mg/l. This stability suggests that the electrolyte's molarity does not significantly influence the Fe concentration if the concentration of HCl is below 1 M.

The apparent increase in Ni concentration with higher molarity levels suggests that Ni ions are more readily dissolving into the solution as the molarity increases. The lowest Ni concentration is 76.50 mg/L in 0.25 M HCL; the highest is 91.88 mg/L in 1 M HCl. This could indicate that higher molarity electrolytes enhance the solubility of Ni or that Ni ions are being more effectively released into the solution due to stronger electrolyte interactions. Higher molarity electrolytes can play a crucial role in enhancing the solubility of nickel ions or facilitating the more effective release of nickel ions into a solution due to more robust interactions with the electrolyte [15]-[17].

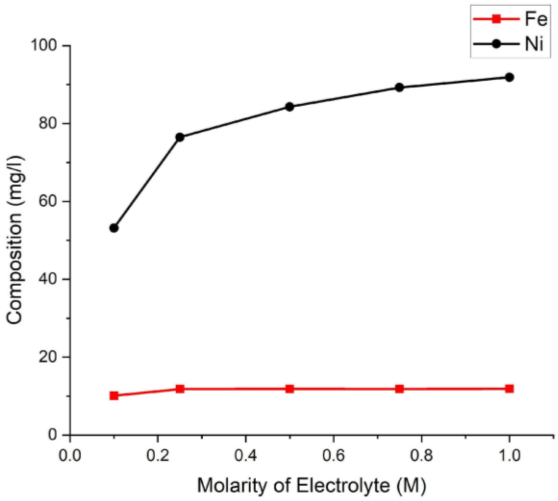

Figure 3. Dissolved Ni and Fe resulting from electrolysis at a 1 V for 2 h voltage were measured using AAS based on differences in electrolyte molarity

Passivation of iron in weak acid media greatly lowers the reaction rates due to the protective oxide layer that develops on the iron surface. This layer prevents further electrochemical activity, hence reducing the dissolution of iron.

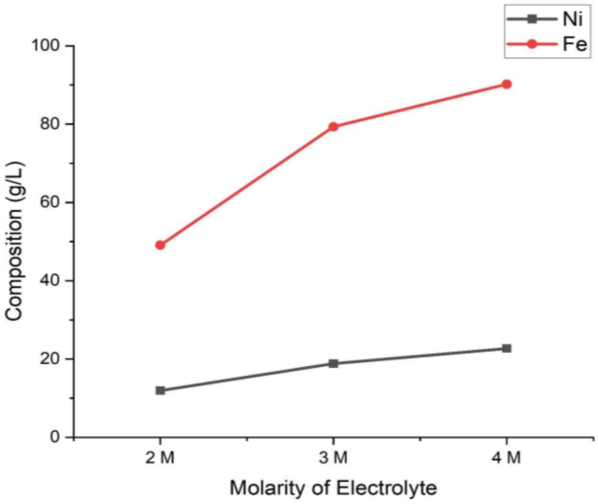

Figure 4. Dissolved Ni and Fe resulting from electrolysis at 2 V for 6 h were measured using 725 ICP-OES based on differences in electrolyte molarity

In contrast, the same acid environment is less aggressive for nickel since it does not form any protective passive layer under these conditions. Consequently, nickel becomes more sensitive to oxidation and dissolution during electrolysis; hence, its higher concentration in solution [18]-[19].

Figure 4 describes the effect of electrolyte molarity on the composition of Ni and Fe in the solution, measured in grams per liter (g/L). The data demonstrate distinct responses of Ni and Fe to changes in the molarity of the electrolyte. For Fe, a positive correlation is observed between the molarity of the electrolyte and the Fe concentration in the solution. Specifically, at 2 M molarity, the Fe concentration is approximately 49.06 g/L.

This concentration increases to about 79.31 g/L at 3 M and 90.17 g/L at 4 M molarity. The trend suggests a linear relationship between the electrolyte molarity and the Fe concentration, indicating that higher molarity levels facilitate more significant dissolution or deposition of Fe in the solution. This phenomenon could be attributed to enhanced ionization or increased availability of Fe ions in higher molarity conditions [20]-[21].

The Ni concentration shows a more modest increase with the electrolyte molarity. At 2 M molarity, the Ni concentration is around 11.95 g/L. The increases to approximately 18.82 g/L at 3 M molarity and to about 22.70 g/L at 4 M. The increment is relatively smaller than Fe, suggesting that Ni is less sensitive to changes in electrolyte molarity. This behavior might be due to the intrinsic electrochemical properties of Ni, such as its standard electrode potential, and because the anode contains almost four times higher percentage of Fe than Ni.

3.2 The Effect of Applied Voltage

The Fe concentration shows slight fluctuations but remains relatively stable across different voltage levels (Fig. 5). In 1 V, it is 11.81 mg/L, and in 8 V, it is 12.28 mg/L, indicating that the applied voltage does not heavily influence the concentration of Fe in the solution. This suggests that voltage changes do not significantly impact Fe ions solubility in 1 M HCl and 2 H electrolysis.

The Ni concentration increases with the applied voltage up to 6V, after which it decreases at 8V. In 6 V, it is 95.57 mg/L, and in 8 V, it is 77.67 mg/L. This indicates a more complex relationship between Ni concentration and applied voltage in 1 M HCl and 2 H electrolysis. The initial increase suggests that higher voltage enhances the solubility or release of Ni ions into the solution [22]-[23]. However, the decrease at 8V may imply a too-rapid reaction because of a too-high voltage, affecting Ni ion concentration at higher voltages [24].

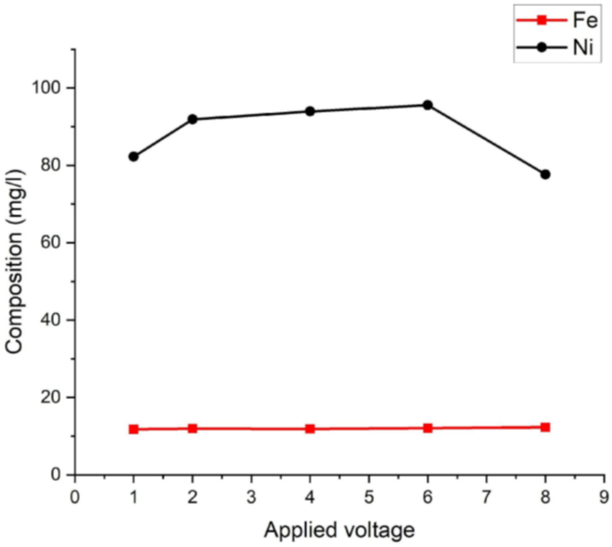

Figure 5. Dissolved Ni and Fe resulting from electrolysis at 1 M HCl for 2 h were measured using AAS based on differences in applied voltage

3.2 Precipitation with NaOH

After the electrolysis process, a filtrate containing metal ions such as Ni^{2}+, Fe^{2}+, Co2+, and others is obtained. The deposition experiment commences with the oxidation of the filtrate solution using hydrogen peroxide (H_2O_2).

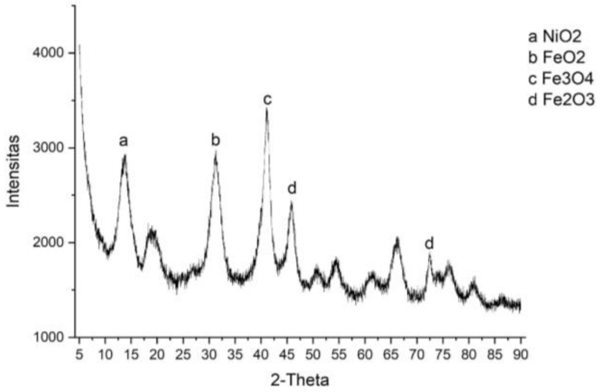

Figure 6. XRD patterns illustrate the precipitates generated at a consistent pH of 4 with reaction temperatures of 50°C, resulting from electrolysis in 2 M HCl at 2 V for 11 hours, with oxidation by H_2O_2 measured using XRD

This oxidation step, crucial for converting Fe^{2}+ ions to Fe^{3}+, is carefully controlled over approximately 1 hour. Following oxidation, the filtrate is subjected to precipitation by adding NaOH and adjusting the pH to approximately 4. Subsequent filtration is then performed to separate the filtrate enriched with Ni^{2}+ and Co^{2}+ ions from the Fe residue. At 50°C precipitation temperature (Fig. 6), the residue exhibits peaks, indicating a mixed-phase composition. Peaks labeled b, c, and d suggest the presence of FeO_2, Fe_3O_4, and Fe_2O_3, with Fe_2O_3 being the dominant phase. Also, there is a small peak of NiO.

Controlling pH and temperature is very important to separate Ni from Fe and other metals that are contained in ferronickel.

4. CONCLUSION

In this investigation, higher molarity levels were associated with increased current, which resulted in faster reaction rates and increased nickel metal solubilization. Ni concentrations increased with increasing molarity, from 76.50 mg/L in 0.25 M HCl to 91.88 mg/L in 1 M HCl. In contrast, Fe content remained fairly constant across multiple molarity levels, ranging from 11.81 mg/L in 0.25 M HCl to 11.95 mg/L in 1 M HCl, demonstrating that molarity has no effect below 1 M. Fe concentration increases significantly as electrolyte molarity increases, from 49.06 g/L at 2 M to 90.17 g/L at 4 M. Ni responds more modestly to changes in high molarity, with concentrations increasing from 11.95 g/L at 2 M to 22.70 g/L at 4 M. The less obvious increase in Ni concentration can be attributed to its intrinsic electrochemical features, such as standard electrode potential, as well as the anode's nearly four-fold higher Fe percentage than Ni. The Ni concentration rises with the applied voltage up to 6 V, reaching 95.57 mg/L, but drops to 77.67 mg/L at 8 V. The initial increase indicates that increased voltage improves the solubility or release of Ni ions into the solution. However, the decline at 8 V could indicate that a high voltage induces an extremely quick response, affecting Ni ion concentration at higher voltages. So, the ideal voltage is 6 volts. The Fe content changes somewhat but remains very consistent across voltage levels.

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