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STUDY ON LEACHING LANTHANUM FROM FERRONICKEL SLAG WITH PRETREATMENT ALKALINE FUSION

Fakhruddin Yudomustafa[1], Eni Febriana[2], Wahyu Mayangsari[2], Nurhayati Indah Ciptasari[2*], Ari Yustisia Akbar[2], Hendrik[2], Soesaptri Oediyani[1], Agus Budi Prasetyo[2]
[1]Department of Metallurgy, Sultan Ageng Tirtayasa University
Jl. Jenderal Sudirman Km 3, Cilegon, Banten, Indonesia 42435
[2]Research Center for Metallurgy, National Research and Innovation Agency (BRIN)
B.J. Habibie Sains and Technology Area, Banten, Indonesia 15314
*Email: nurh024@brin.go.id

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Abstract

Ferronickel slag is a byproduct of nickel ore smelting. Several efforts have been made to find alternative applications for ferronickel slag, such as the production of construction materials, cement, or geopolymers. It is reported that 38% is used for road construction, 48% is used for industrial cement mixtures, and the rest is used for fertilizers, geopolymers, and hydraulic techniques. Ferronickel slag still contains some valuable minerals such as silica, magnesium, nickel, iron, and several REEs (rare earth elements). One of the REEs, namely lanthanum, has many applications, including Ni-MH (nickel-metal hydride) batteries, phosphors for lamps, fluid-cracking catalysts for oil refining, LaNi5 for hydrogen gas storage, metal alloys for cast iron, steel and magnesium alloys, additives for glassware (for cameras), and lanthanum hexaboride ceramic. In connection with the slag, which contains impurities in strong silica compounds, it is necessary to carry out an alkaline fusion treatment. Alkaline fusion was carried out by varying the time from 0.5 to 4 hours and the ratio of the mass of slag to NaOH: 1:0.6, 1:1, 1:1.23, 1:1.47, and 1:1.84. The biggest decrease in SiO_2 *was in the 3-hour alkaline fusion time, from 48.347% to 27.3%, and in the mass ratio at 1:1.47, from 48.347% to 21.413%. This research aims to provide added value for ferronickel slag by extracting lanthanum by acid leaching using* H_2SO_4 *reagent by varying the time (5, 10, 30, 60, and 120 minutes), temperature (30, 60, and 90 °C), and concentration (1, 2, and 3 M). The results showed that the best leaching point was at 5 minutes, 30 °C, and 1 M, yielding a lanthanum extraction percentage of 38.082%.*

Keywords: *Acid leaching, added value, alkali fusion, ferronickel slag, lanthanum*

1. INTRODUCTION

Ferronickel slag is a byproduct of nickel ore smelting. Ferronickel slag is designated as hazardous and toxic waste for the environment with a danger level 2 (i.e., it has delayed effects and does not directly influence humans) by Government Regulation (PP) Number 101 of 2014. Therefore, based on the Ministerial Regulation of the Ministry of Environment and Forestry, Chapter I, Article 2, storage and disposal of B3 waste are required. Currently, Ferronickel slag is only used as a construction material and is merely piled in one place [1]. Numerous attempts are underway to find alternate uses for ferronickel slag, including the creation of cement, geopolymer, and building materials [2].

Reported that the main compound in ferronickel slag was silica in the form of SiO_2 at 45.69%. Based on XRD (x-ray diffraction) analysis [3], ferronickel slag is dominated by magnesium silicate and iron silicate, which are formed by forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$), and fayalite (Fe_2SiO_4). To form an amorphous structure, the furnace's slag can be

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cooled using air cooling or granulation techniques [4].

Ferronickel slag retains important minerals, including silica, magnesium, nickel, iron, and several REEs (rare earth elements). The main components of ferronickel slag are silica (Si) at 30%, magnesium (Mg) at 20%, iron (Fe) at 12%, and aluminum (Al) at 1-2%, along with other elements [1]. A study [3] reported that the REEs contained ferro-nickel slag. Lanthanum, a rare earth element, is used in a variety of products, such as phosphor for lamps, fluid-cracking catalysts for oil refining, $LaNi_5$ for storing hydrogen gas, metal alloys for cast iron, steel, and magnesium, glass additives (for cameras), and lanthanum hexaboride ceramic [5].

Regarding slag containing impurities in the form of strong silica compounds [6], the separation of silica is very important in improving the recovery of valuable metals from ferronickel slag [2]. Several treatments have been conducted [7] with the caustic leaching process under NaOH concentration 5 N, temperature 80 °C, and time 4 hours, resulting in a soluble silica content of 18.4%. Alkali pugging with slag conditions: NaOH mass ratio 1:2, temperature 250 °C, and time 4 hours resulted in a soluble silica content of 35.2%. Alkali fusion with slag conditions: NaOH mass ratio 1:1, temperature 650 °C, and time 4 hours resulted in a soluble Si content of 35-37%. Another study was conducted by [8] with alkali fusion treatment on zircon tailings with a sample size of 180 mm, a temperature of 450 °C, a duration of 3 hours, and a mass ratio of 1:1, resulting in a dissolved Si content of 66%. Alkali fusion is classified as wet decomposition, which involves the addition of a base (commonly NaOH) followed by heating at a specific time and temperature [6].

In this study, alkali fusion treatment was performed on samples by varying the alkali fusion time of 0.5, 1, 2, 3, and 4 hours and the mass ratio of slag: NaOH 1:0.6; 1:1; 1:1.23; 1:1.47; and 1:1.83 to initially study the effect of temperature and duration on alkali fusion to reduce SiO_2 content. The sodium silicate created during the alkali fusion process was dissolved by water leaching, which increased lanthanum in the water-leaching residue. This is anticipated to be used as a reference for thermodynamic factors in the alkali fusion process for handling ferronickel slag.

Additionally, this research aims to add value to ferronickel slag by leaching with sulfuric acid (H_2SO_4) reagent to recover lanthanum metal. The selection of H_2SO_4 reagent in acid leaching was based on research on lanthanum leaching from a hydrocracking catalyst. The result was that lanthanum recovered 90.836% [9]. According to the study on the leaching of REEs from tin slag II, the percentage of extraction increases as the temperature rises between 30 and 90 °C [2]. The study's findings on the influence of reagent concentration showed that using H_2SO_4 reagent to leach lanthanum from red mud enhanced recovery as concentration increased between 1 and 3 M [10]. The effect of time-based leaching REEs from tin slag II was then varied to 5, 10, 30, 60, and 120 minutes; the resulting leaching occurred in rapid time [2].

2. MATERIALS AND METHODS

2.1 Materials

The raw materials used in this research are ferronickel slag collected from PT ANTAM Pomaalaa. A ball mill milled the ferronickel slag to obtain a -200 particle size mesh. Characterization of ferronickel slag used XRD to determine the phase formed in ferronickel slag. XRF is used to determine the chemical composition of ferronickel slag. ICP-OES to determine rare earth elements in ferronickel slag, especially lanthanum.

2.2 Methods

The experiment was executed in three phases: acid leaching, water leaching, and alkaline fusion. The investigation uses ICP-OES (inductively coupled plasma-optical emission spectrometry), XRD (x-ray diffraction), and XRF (x-ray fluorescence) as analytical methods [2].

2.3 Alkali Fusion

Alkali fusion mixture of ferronickel slag: NaOH by physical blending. The mixture sample was weighed and put into the crucible. The sample was performed in a muffle furnace. This research employed time variations of alkali fusion (30, 60, 120, 180, and 240 minutes) and mass ratio modifications of ferronickel slag with NaOH (1:0.6; 1:1; 1:1.23; 1:1.47; 1:1.84). The alkali fusion temperature was established at 150 °C.

2.4 Water Leaching

Product alkali fusion named frit was then water leached using distilled water with a conditioning temperature of 90 °C, leaching time of 60 minutes, and S/L 1/5 g/mL. Water leaching aims to dissolve silica as sodium silica from alkali fusion. Filtrate and residue are the end products of the water-leaching process. After water leaching, the sample was filtered to separate the filtrate and residue. The residue from the leaching of water, which will be used as raw material for leaching, is dried using an oven at 105 °C, and the filtrate from the leaching is analyzed by ICP-OES analysis to determine the level of dissolved impurities during the water leaching process.

2.5 Acid Leaching

The residue is dissolved with H_2SO_4 and placed in the reactor glass to begin the acid-leaching process. Solid/Liquid (S/L) 10/100 g/mL, 200 rpm stirring rate, concentration variations of 1, 2, and 3 M, followed by variations in leaching duration for 5, 10, 30, 60, and 120 minutes, and temperature variation for 30; 60; and 90°C, were the conditions under which acid leaching was conducted. After acid leaching, filtration was carried out to produce filtrate in the form of PLS (pregnant leaching solution) and residue. The filtrate was examined via ICP-OES, whereas the residue was assessed using XRF.

3. RESULTS AND DISCUSSION

3.1 Characterization of Ferronickel Slag

Table 1 presents the findings of the characterization of the first ferronickel slag via XRF analysis.

Table 1. The result of the characterization of ferronickel slag using XRF analysis

Compounds	Wt.%
SiO_2	48.347
Cr_2O_3	1.931
Al_2O_3	5.946
MgO	27.263
Fe_2O_3	13.427
Others	3.084

The dominant compounds in ferronickel slag are SiO_2, MgO, and Fe_2O_3, which are 48.347%, 27.263%, and 13.427%, respectively.

Table 2. The result of the characterization of ferronickel slag using ICP-OES analysis

Element	Wt (ppm)
Ce	1109
La	347
Nd	303
Pr	71
Y	112
Sm	116

This is consistent with several previous studies that state that the most dominant composition in ferronickel slag is silica oxide [11]-[14].

Table 2 presents the characterization results of the first REEs, particularly lanthanum (La), in the initial ferronickel slag, revealing a concentration of 347 ppm of lanthanum.

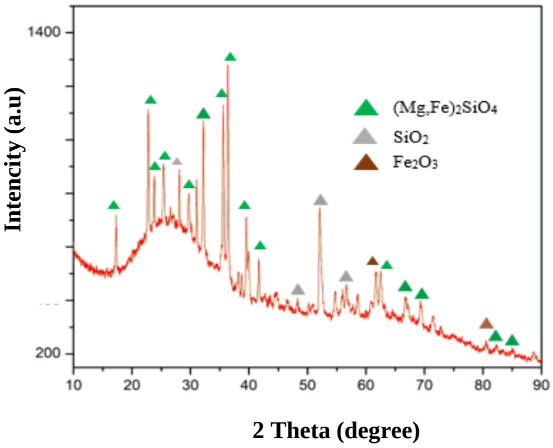

Figure 1. The result of the characterization of ferronickel slag used XRD analysis

Figure 1 illustrates the outcomes of the characterization of preliminary ferronickel slag using XRD analysis. In line with earlier research, the primary components that predominated in ferronickel slag were olivine $(Mg,Fe)_2SiO_4$, silica (SiO_2), and hematite (Fe_2O_3) at the main phase [15]-[17].

3.2 Alkali Fusion

3.2.1 Effect of Time on SiO_2 Removal

The effect of time on SiO_2 removal after alkaline fusion is shown in Fig. 2. The effect of time on the results of SiO_2 levels is that the longer the alkali fusion time, the greater the SiO_2 in ferronickel slag reacts with NaOH to form Na_2SiO_3. This phenomenon is due to the principle of the reaction rate, namely, the reactant decreases with increasing time, and the product increases as time increases time [18].

However, after 240 minutes, there was an increase from 27.3% to 27.4%. This is possible because after 3 hours, the reaction reaches equilibrium, making it reversible, so Na_2SiO_3 is converted back to SiO_2. This phenomenon can be proven by finding the equilibrium constant value using the reaction equation: $K_P = K_c\,(0{,}0821T)^{\Delta n}$, with the explanation: Kp = Gas equilibrium constant, Kc = Reaction equilibrium constant, T = Temperature (Kelvin), and Δn = Change in reaction moles.

After calculations, it was found that the value of Kp is 4.70, and after further calculations, the value of Kc was found to be 0.135. It is known that the value of Kc << 1, so if the reaction has reached equilibrium, the reaction will shift to the left (reactants) [18].

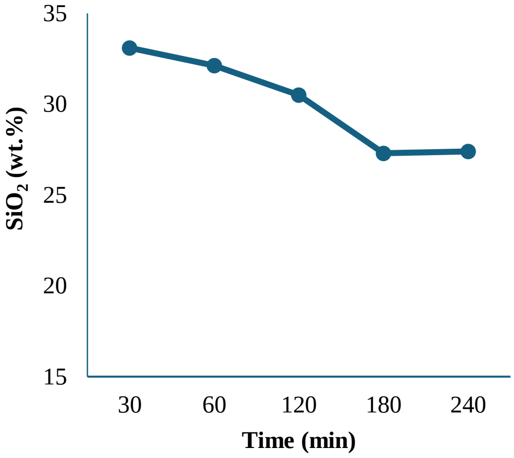

Figure 2. Effect of time on SiO_2 removal

It can be concluded that after an equilibrium time of 3 hours, the reaction will shift towards the reactants, increasing the mass of SiO_2.

3.2.2 Effect of Mass Ratio on Removal of SiO_2

The effect of mass ratio on the removal of SiO_2 after alkaline fusion is shown in Fig. 3. The result is that after a mass ratio of 1:1, there was a significant decrease in SiO_2 to a mass ratio of 1:1.47 and an increase of 1:1.83. In Figure 3, there is an increase in SiO_2 content from a mass ratio of 1:0.6 to 1:1, which is inconsistent with the theory that adding a larger number of reactants results in a larger amount of product [18]. However, after the mass ratio of 1:1, there is a significant decrease in SiO_2 content until the mass ratio of 1:1.47, followed by an increase at 1:1.83.

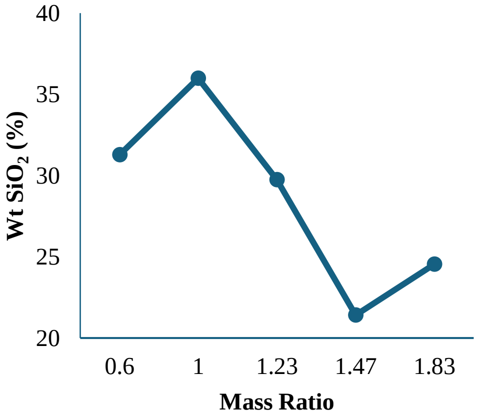

Figure 3. Effect of mass ratio on SiO_2 removal

The significant removal at 1:1.47 occurs because, according to stoichiometric reactions, the moles needed to react with 1 mole of SiO_2 are 2 moles of NaOH or a mass ratio of 1:1.32. At the mass ratio of 1:1.47, the stoichiometric reaction is 1:2.2 moles, so it can be assumed that SiO_2 is converted optimally or the reaction has reached equilibrium. After 1:1.47, there is an increase in SiO_2 content because the reaction is reversible, leading to a tendency for Na_2SiO_3 to form SiO_2. This phenomenon is evidenced by the value of Kc >> 1, where, according to Le Chatelier's principle, if the value of Kc >> 1 after the reaction reaches equilibrium, then with the addition of NaOH, the reaction will shift to the left (reactants) [18].

3.3 Acid Leaching

3.3.1 Effect of Leaching Time on Percent Extraction

Figure 4 shows the effect of time on percent extraction. Acid leaching occurs relatively quickly because lanthanum has a relatively high electronegativity [2], which allows it to easily release electrons and dissolve in H_2SO_4.

In Figure 4, it is observed that the longer the leaching time, the lower the extraction percentage, but this does not occur at a temperature of 90 °C. To determine the effect of leaching time, it is necessary to determine the Kc value, which can be expressed with the equation:

$$K_c = \frac{[La_2(SO_4)_3][H_2O]^6}{[H_2SO_4]^3[La(OH)_3]^2}$$

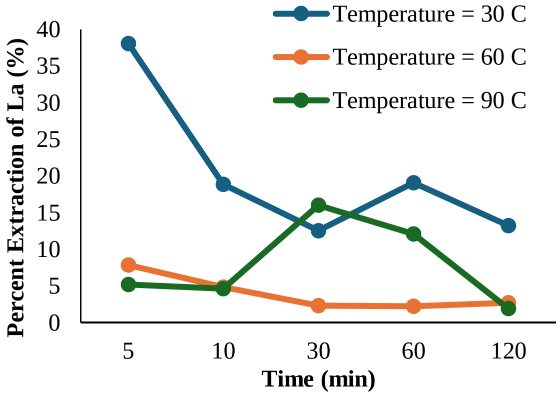

Figure 4. Effect of leaching time on the percent extraction of Lanthanum

After the calculations were performed, it was found that the Kc value was 21.33. If the value of Kc >> 1, then when the reaction reaches equilibrium, the reaction will shift to the right (products) [18]. Additionally, the obtained results do not align with the principle of reaction rate, which states that "reactants decrease over time while products increase over time," as shown in equation [18]. Figure 4 shows that lanthanum leaching occurs relatively quickly because lanthanum has a relatively high electronegativity [2], making it easy to release electrons and thus dissolve in H_2SO_4. The electronegativity of lanthanum is 1.117 [19].

In Figure 4, it is known that the longer the time, 5 minutes is the best time for leaching at temperatures of 30 and 60 °C, but this does not occur at 90 °C because at 90 °C the Si content in the filtrate is higher compared to 30 and 60 °C. The filtrate's Si content at 30 to 90 °C is 59490, 27796, and 73193 ppm, respectively. The research concluded that the best time for lanthanum leaching is 5 minutes, so this time was set as the time for subsequent leaching.

3.3.2 Effect of Temperature on Percent Extraction

Leaching was carried out by varying the temperature to 30, 60, and 90 °C, and the leaching time was 5 minutes, S/L 1/10, stirring rate 200 rpm, and H_2SO_4 concentration of 1 M. The Effect of temperature on percent extraction is shown in Fig. 5. Increasing temperature decreases the percentage of lanthanum extraction. This phenomenon is due to the solubility value. The solubility value of the product ($La_2(SO_4)_3$) decreases with increasing temperature. The solubility values of the product, respectively, from 30 to 90 °C, are 1.90, 1.26, and 0.79 [20]. Consequently, it can be determined that the optimal temperature for lanthanum leaching is 30 °C.

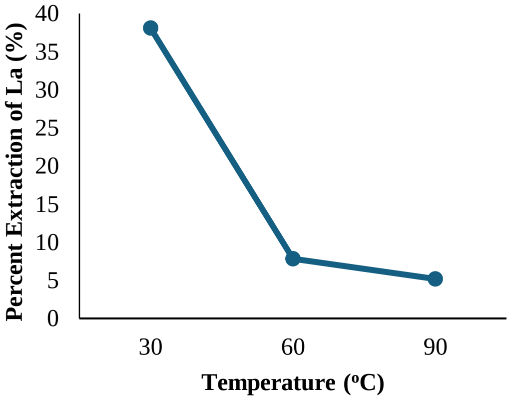

Figure 5. Effect of leaching temperature on the percent extraction of Lanthanum

3.3.3 Effect of H_2SO_4 Concentration on Percent Extraction

The leaching process occurs at 30 °C, utilizing a solid-to-liquid ratio of 1:10, a duration of 5 minutes, an agitation speed of 200 rpm, and H_2SO_4 concentrations of 1, 2, and 3 M.

Figure 6 shows the effect of concentration on percent extraction**.** The higher the concentration of H_2SO_4**,** the lower the percentage of lanthanum extraction.

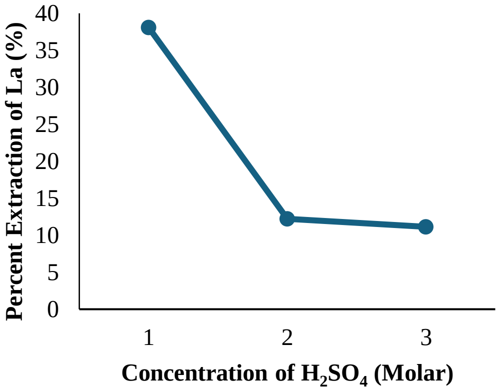

Figure 6. Effect of leaching concentration on the percent extraction of Lanthanum

Figure 6 illustrates that an increase in H_2SO_4 concentration correlates with a decrease in the percentage of lanthanum extraction. The results obtained in this study do not align with the research on the leaching of La from red mud using H_2SO_4 reagent, where a lower pH of the solution used leads to a decrease in extraction percentage [10].

The calculation was performed using equation [18]: $pH = -\log[H^+]$. The H^+ is the concentration of H_2SO_4 used. Thus, the pH presented in Table 3 is obtained. It can be concluded that the best leaching was done at an H_2SO_4 concentration of 1 M.

Table 3. Convert concentration to pH

H2SO4 Concentration	pH
1	-0.30
2	-0.60
3	-0.77

4. CONCLUSION

The duration of alkali fusion time and the slag: NaOH mass ratio affect the influence of SiO_2. The largest decrease in alkali fusion time of 3 hours is from 48.347% to 27.3%, and in the mass ratio of 1:1.47, it is from 48.347% to 21.413%. Time, temperature, and concentration influence the leaching of lanthanum. The duration of time inversely affects the extraction percentage, except for a temperature of 90 °C. The impact of temperature is such that an increase in temperature results in a decrease in extraction percentage. The impact of concentration is that an increased concentration results in a diminished extraction percentage. The optimal leaching point is at 5 minutes, 30 °C, and 1 M, resulting in a lanthanum extraction percentage of 38.082%.

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