Simulation of precious metals recovery from nickel smelter slag under high-pressure oxidative acid leaching (HPOXAL)

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Abstract. The nickel smelter slag as a solid waste of pyrometallurgical operations can be harmful to the environment especially against the ground that will be contaminated by hazardous components contained the smelter slag. Nickel smelter slag has the content of valuable metals as the following: Nickel (Ni), Cobalt (Co), Copper (Cu), Iron (Fe) and Zinc (Zn). Those valuable metals were carried out by high-pressure oxidative acid leaching to recover all the valuable metals suitable with the high measures of recovery. High-pressure oxidative acid leaching (HPOXAL) is a suitable process for the nickel smelter slag with the parameters of the leaching process as the following: the particle size about – 150 + 74 μm, sulfuric acid solution with the concentration of 0.3 mol in 1 liter solution, Ratio of Liquid to Solid (L/S) with 7 ml of liquid to 1 gram of solid components, oxygen overpressure at 600 kPa, operating temperature about 180 - 200 °C and the retention time of 80 minutes. The measures recovery of this leaching process for each valuable metal in percent of initial weight such as nickel and cobalt about 97%, copper about 95%, 94% of zinc and all iron can be separated, respectively. At the separation section, LIX 984N as extractant extracts copper from the product (leaching solution) of the reactor, limestone was used to capture iron in the leaching solution, versatic 10 and decyl-4PC were conducted to remove undesirable mineral that was generated from the leaching process, and cyanex 272 extractants to extract such as nickel, cobalt, and zinc, respectively. This simulation used the feed flowrate with 150 tons per day. The results of the precious metals product were generated each the mass rate such as copper, nickel, cobalt, zinc, and iron with 927 kg/day, 2147 kg/day, 875 kg/day, 199 kg/day and 71,000 kg/day, respectively.

1. Introduction

The particular reason of this case is caused huge quantities of nickel smelter slag as a waste of pyrometallurgical operations by the metal industries. In 2017 according to USGS mineral resources program that amount of world nickel-mine production was by 2.1 million metric tons of nickel, in which Indonesia gave contributing for nickel-mine production by 400,000 metric tons of nickel or about 19% of world nickel-mine production. In statistic of USGS mineral resources program also showed increasing the nickel-mine production in Indonesia which previously produced 199,000 metric tons of nickel in 2016 [1]. Based on the result that shows increasing nickel-mine production while it definitely increases nickel which it is called nickel smelter slag. The slag is dumped continuously around the world that is averagely 50-200 tons of smelter slag every day in each pyrometallurgical metal industry, it has an appearance like gravel with the particle size ranging from 12-75 mm of particle size.
As solid waste, the nickel smelter slag can be harmful to the environment especially against soil that will be contaminated by hazardous components contained the smelter slag. The prime risks posed by these contained metals are they’re hazardous, their persistence or inability to degrade chemically or biologically in the environment, and their tendency to bio-accumulate in the food chain. Humans, being on top of the food chain, receive the most impact in the form of both chronic and acute health problems with their increasing health care costs and declining productivity. The slag contains appreciable amounts of base metals such as nickel (Ni), cobalt (Co), copper (Cu), iron (Fe) and zinc (Zn) in particular. Hence, as the great way to solve the problem, the nickel smelter slag is reused to gain the precious metals under suitable process which an effective and economical way is needed to recover the precious metals.

Nowadays, Leaching is generally process used to reutilize and reduce the nickel smelter slag. There are various methods that have been developed for the extraction of precious metals from slag. Atmospheric leaching is a hydrometallurgical method which is early applied to extract the entrapped precious metals from various smelter slags. However, though most of the cobalt, nickel, zinc, and copper in smelter slag could be leached with lixiviants such as aqueous sulfur dioxide and acid, subsequent treatments including solid-liquid separation and recovery of metals are greatly difficult, because there happened iron co-extraction and silica gel formation as by-product from the leaching [2]. Therefore, researches have intended more on high-pressure oxidative acid leaching of slag by adding an auxiliary oxidant as far as possible to minimize the influences resulting from iron and silica gel formation.

High-pressure oxidative acid leaching (HPOXAL) process has received considerable attention from researchers who are interested in recovering precious metals from smelter slags. It is considered as the best option in terms of selective dissolution of precious metals such as Ni, Co, Cu, Zn and iron from nickel smelter slag. In this study, the optimum condition of HPOXAL process uses parameter according to Feirong Huang about the Selective recovery of valuable metals from nickel converter slag at elevated temperature with a sulfuric acid solution [2]. By using Aspen HYSYS application, it can show accurately the result of manufacturing simulation before this design will be implemented as the real plant. The amount of smelter slag flowrate was used in this simulation by 150 tons per day that is equivalent to 6,250 kg per hour.

2. Materials and methods
A huge quantity of slag, which is a waste by-product of smelting and converting operations in pyrometallurgical plants, is posing a potential environmental threat due to entrained values of precious metals and sulfur. The nickel smelter slag has various contents such as Ni, Cu, Co, Zn, and iron, in general. The contents of the nickel smelter slag are shown in Table 1, like the below.

| Contents   | % weight |
|------------|----------|
| Nickel (Ni)| 1.475    |
| Cobalt (Co)| 0.601    |
| Copper (Cu)| 0.650    |
| Iron (Fe)  | 47.340   |
| Zinc (Zn)  | 0.141    |

There are still many the precious metals contained in the nickel smelter slag that can be recovered with considering an economic point of view to fulfill the increasing demand of nickel, copper, cobalt, zinc, and iron in the world. The metal-mine sources will deplete if all metals demand only relies on the mining sources. This is a great solution to reduce the waste slag harm effect against the environment.
and mining production cost, to reach the target it must be followed with a suitable method for metals recovery from the nickel smelter slag.

High-pressure oxidative acid leaching (HPOXAL) process is the most suitable for recovery of precious metals in nickel smelter slag. HPOXAL of nickel smelter slags was investigated as a process to facilitate slag cleaning and selective dissolution of precious metals for economic recovery. The recovered measure for the process by each precious metals as the following; nickel and cobalt recovered by 97% of initial weight, copper recovered by 95% of initial weight [2], zinc recovered by 94% of initial weight, and almost all iron dissolution [3], respectively.

Five key parameters, namely; operating temperature, acid addition, oxygen overpressure, solids loading (solid-liquid ratio) and particle size, were examined on the process performance [4]. The optimum parameters are used in this study which is shown in Table 2, like the following.

**Table 2. Parameters for precious metals recovery from nickel smelter slag [2].**

| Parameters                | Values                 |
|---------------------------|------------------------|
| Particle size             | -150 +74 μm            |
| Acid concentration (H₂SO₄) | 0.3 mol/liter          |
| Liquid-Solid ratio        | 7 ml/gram              |
| Oxygen overpressure       | 600 kPa                |
| Operating temperature     | 180-200°C              |
| Time                      | 80 minutes             |

![Flowsheet of precious metals recovery from nickel smelter slag.](image)

**Figure 1.** Flowsheet of precious metals recovery from nickel smelter slag.

The flowsheet on Figure 1 shows a process flow diagram to extract and recover precious metals from nickel smelter slag. The system has a design based on the CSIRO DSX process [5-6], nevertheless, it is added several combinations and an additional process of extraction to reach the result of precious metals, particularly for copper, nickel, cobalt, zinc, and whereas iron is separated and captured by limestone.
the first flow or raw material input, cooled nickel smelter slag generally has a particle size in the range 12-75 mm which it is crushed by crushing instrument with the type of double-roll crusher. The crusher has the capability of reduction ratio by 4:1, the reduction ratio means that the particle size can be crushed four times smaller than the initial particle size. Grinding instrument of ball mill type and dry-sieve or vibrating screens are also used to achieve desired particle size by -150 +74 μm.

HPOXAL is the main process to leach the nickel smelter slag. The process is carried out in the autoclave which the slag blends with sulfuric acid (H₂SO₄) concentrated by 0.3 mol per liter, the liquid-solid ratio by 7 ml per gram, 600 kPa of oxygen overpressure, and 180-200 °C of operating temperature. The leaching process takes time during 80 minutes to achieve optimum precious metals recovery.

The purification step for each precious metal happen in the solvent extraction, it uses some suitable extractants which depend on extracted precious metal such as; LIX 984N extractant is used to extract copper from leaching effluent, Cyanex 272 extractant is used to extract cobalt and zinc, Versatic 10 extractant and Decyl-4PC synergist are used to remove other mineral or contaminant which it obstructs separating in cobalt and zinc solvent extraction (Co/Zn SX). Iron is separated in the neutralization by limestone (CaCO₃).

Electrowinning also called electroextraction is used to capture the precious metals from extractant solution or concentrated precious metals electrolyte by electrical charge and anode plates. Thus, the precious metals finally produce as cathode plate. Every single precious metal needs different anode in electrowinning process, such as; copper uses Pb-Ca-Sn anode, nickel uses Pb alloy (99% Pb, 0.6% Sn, 0.05% Sr) anode, zinc uses Lead-Silver (0.55%) anode, and cobalt uses DSA anode [7].

3. Results and Discussion

The simulation of precious metals recovery from nickel smelter slag is conducted with Aspen HYSYS software. Particularly, HPOXAL process is focused to be simulated because this process determines the measure of recovered precious metals. According to Figure 2 that shows the three streams as input stream forward to leaching reactor which oxygen stream is previously compressed to reach 600 kPa overpressure of oxygen, further, the cooler decreases temperature the gas stream from the compressor till the temperature of the stream goes down to operating temperature around 200 °C. The nickel smelter slag stream is a crushed slag which it has crushed and grounded by double-roll crusher, grinding instrument of ball mill type, and filtered by vibrating screens. The quantity of nickel smelter slag is processed in this simulation by 150 tons of nickel smelter slag. Sulfuric acid has a function as reactant during HPOXAL process.
Table 3. Material streams of high-pressure oxidative acid leaching (HPOXAL) process.

| Compounds         | Streams (kg/h) | Nickel smelter slag | Sulfuric acid | Oxygen | Leaching effluent | Vapor |
|-------------------|----------------|---------------------|---------------|--------|------------------|-------|
| FeSO₄             | 2958.750       | 0                   | 0             | 0      | 0                | 0     |
| Fe₂(SO₄)₃        | 41.250         | 0                   | 0             | 0      | 0                | 1547.380 |
| NiO               | 92.500         | 0                   | 0             | 0      | 14.971           | 2.062 |
| ZnO               | 9.375          | 0                   | 0             | 0      | 0                | 0.562 |
| CuO               | 38.125         | 0                   | 0             | 0      | 1.547.380        | 1.144 |
| SiO₂              | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| Fe₂O₃             | 23.325         | 0                   | 0             | 0      | 0                | 0     |
| CuSO₄             | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| NiSO₄             | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| ZnSO₄             | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| CoSO₄             | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| H₂SiO₄            | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| H₂SO₄             | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| H₂O               | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| O₂                | 19.471         | 0                   | 0             | 0      | 0                | 0     |
| **Sum**           | 6250.000       | 44322.930           | 160.000       | 7680.868 | 43052.062        |       |
| **TOTAL**         | 50732.930      | 50732.930           | 50732.930     | 50732.930 | 50732.930        |       |

Operating conditions of the HPOXAL process are determinant to the reaction path. Based on the operating condition which has been chosen as the main method of HPOXAL process, it occurs several complicated reactions. For the reaction path of iron occurs according to the following reactions:

\[2\text{FeSO}_4 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}\]  \hspace{1cm} (Eq.1)

\[\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4\] \hspace{1cm} (Eq.2)

For the reaction path of other precious metals (Me = Cu, Ni, Zn, and Co):

\[2\text{MeO} + \text{SiO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{MeSO}_4 + \text{H}_4\text{SiO}_4\] \hspace{1cm} (Eq.3)

The measurement of recovered precious metals is shown in Table 3 that the quantities of recovery for each precious metal such as copper, nickel, zinc, cobalt, and iron are 95%, 97%, 94%, 97% of initial weight and all iron is involved in the reaction, respectively. The result shows that HPOXAL process is the promising process to reutilize the nickel smelter slag with high conversion.

4. Conclusions

Nickel smelter slag is abundantly available in the disposal of metal industries, especially pyrometallurgical industries. There are many harmful effects on the environment as well as for human’s health. Recovery or extraction of precious metals is contained in the nickel smelter slag that is as the greatest way to solve the problem. High-pressure oxidative acid leaching (HPOXAL) is the most suitable and promising process to achieve the highest measure of the dissolving into the leaching solution. The parameters for the HPOXAL process are particle size -150 +74 μm, H₂SO₄ concentration 0.3 mol/liter, oxygen overpressure 600 kPa, Liquid-Solid ratio 7 ml/gram, operating temperature 180-200°C and time 80 minutes. By the operating conditions that precious metals such as 95% of copper, 94% of zinc, and
97% of nickel and cobalt can be dissolved into the leaching solution. Further, the purification step using CSIRO DSX process can produce to each precious metal in the high-grade cathode. The quantity of nickel smelter slag is processed in this simulation by 150 tons of nickel smelter slag which it can produce high-grade cathode by 927 kg/day of copper, 2147 kg/day of nickel, 875 kg/day of cobalt, 199 kg/day of zinc and 71000 kg/day of iron, respectively.

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