Nickel-copper matte leaching process under atmospheric conditions

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Abstract

Nickel-copper mattes are conventionally treated by pyrometallurgical method, later the hydrometallurgical processes have gained an advantage over the conventional one by recovering valuable metals and reducing the environmental impact of industrial activities related to the processing of nickel ore deposits. As a mean of getting insight in the progress of a chemical process, computer simulation is a cost effective mean through which the effects of process variables such as flow rates and operating conditions variations can be assessed at the design phase. This study case deals with modeling and simulation of atmospheric leaching process of nickel-copper matte. To understand the nature of the leaching process during the stage of operation, the leaching mechanism of the matte is explained based on chemistry. Through simulation the effects of different parameters on nickel leaching process were investigated, mainly operating temperature, and acid concentration. The modeling of this process was performed on a computer simulation package known as Aspen Plus. Under atmospheric pressure 60.35% of nickel, 9.40% of iron, 17.02% of copper, 7.80% of cobalt and 2.5% of zinc are extracted under suitable conditions of sulfuric acid concentration and reaction temperature.

1. Introduction

Conventionally, nickel-copper mattes are treated by pyrometallurgical method, but later the hydrometallurgical processes have gained an advantage over the conventional one by recovering valuable metals and reducing the environmental impact of industrial activities related to the processing of nickel ore deposits [1]. At industrial scale, nickel has strategic importance due to its extensive application in foundry, producing stainless steel, alloy, battery, and catalyst [2]. Recently, relatively great attention has been paid to the research on the recovery of nickel from secondary resources: spent catalyst [3], waste battery [4, 5] and tailings [6]. Commonly, nickel is found in iron meteorites as the alloys kamacite and taenite. Nickel ores are of two types [7]: (1) Primary sulphide deposits associated with mafic and ultramafic rocks, (2) Near-surface laterite deposits formed over olivine-rich host rocks following intense weathering. The sulphide ores have been the major source of nickel; however, the lateritic ores have been estimated to constitute about 73% [8] of the known nickel reserves of the world. According to the latest data by the USGS, world nickel reserves amount to 80,000,000 metric tons [9]. Refer to high nickel production costs associated with traditional pyrometallurgical techniques and the depletion of high-grade sulphide ores, new interest has been developed concerning the production of the nickel and cobalt by high pressure acid leaching (HPAL) of nickel laterites. Industrial leaching processes generally comprise multiple leaching in autoclaves that accommodate 3phase (solid-liquid-gas) systems that exhibit complicated chemistry and kinetics. So, it is essential that these processes operate optimally to ensure maximum refinery throughput [10]. Understanding how changes in process and operating conditions influence the performance of the leach process, is of paramount importance in arriving at this state of operation; hence our work lines in this perspective.

2. Nickel processing and leaching mechanism

Conventionally, two process routes are employed for leaching Ni-Cu matte. The first one involves both atmospheric and pressure leaching in acidic nickel-copper sulphate solution, with oxygen being the oxidizing agent. In this process the matte is first leached under atmospheric conditions followed by a pressure leaching step, and in both steps O₂/air is splashed into the leaching vessels. During atmospheric leaching substantial quantities of nickel and cobalt are dissolved while copper and iron

are precipitated from the solution, and any platinum group metals (PGM) present remains solids. The precipitated copper and any unleached nickel and cobalt are dissolved in the subsequent pressure leaching step or, in some cases, fed to a smelter.

The other leaching process route employs a pre-leach step, which is essentially a matte repulping step, prior to a pressure leaching step. This process is considered to be basically a non-oxidative atmospheric leach stage since leaching of the matte starts immediately after it comes into contact with the $CuSO_4$ - H_2SO_4 repulping solution. During the pre-leaching stage nickel, iron and cobalt are partially dissolved, while the copper is precipitated. In both of these Ni-Cu matte process route alternatives, nickel and cobalt can be recovered from the solution as metal by electrowinning or hydrogen reduction, or they may be recovered as sulphate crystals. Copper can be recovered as metal by electrowinning from the sulphate solution or by electrorefining if the precipitated copper was produced by the smelting process [11]. This case study deals with the leaching of nickel-copper matte. The principal phases present in the matte are metallic nickel (Ni^o), millerite (NiS), metallic copper (Cu^o), chalcocite (Cu₂S), CuS, metallic cobalt (Co^o), metallic zinc (Zn^o), metallic iron (Fe^o) and pyrrhotite (FeS), Pyrite (FeS2). Nickel contributes to approximately 65% of the total particulate feed.

For the Ni-Cu matte leached in acidic solution, CuSO₄-H₂SO₄-O₂, and the characterization of the leaching liquor and residues [11-13], the mechanism is the leaching of metals with simultaneous precipitation of aqueous copper via the cementation process and the atmospheric pressure oxidative dissolution in the sulfuric acid. The actual reacting system is a much more complex series-parallel reaction network involving the oxidation of metals and the progressive oxidation of sulfides. For cementation process, metallic nickel is being leached according to reaction (1). The dissolution of metallic iron precedes the well-known reaction of cementation of copper by metallic iron [14], reaction (2).

$$Ni^{o} + CuSO_{4} \rightarrow Cu^{o} + NiSO_{4}$$

$$Fe^{o} + CuSO_{4} \rightarrow Cu^{o} + FeSO_{4}$$

$$(1)$$

In the presence of air the minerals are leached through an oxidative dissolution in the sulphuric acid according to the following reactions:

$$Ni^{0} + H_{2}SO_{4} + 1/2O_{2} \rightarrow NiSO_{4} + H_{2}O$$
 (3) $2Cu^{o} + H_{2}SO_{4} + 1/2O_{2} \rightarrow Cu_{2}SO_{4} + H_{2}O$ (6) $E^{0} + H_{2}SO_{4} + 1/2O_{2} \rightarrow EOSO_{4} + H_{2}O$ (7) $E^{0} + H_{2}SO_{4} + 1/2O_{2} \rightarrow EOSO_{4} + H_{2}O$ (7) $E^{0} + H_{2}SO_{4} + 1/2O_{2} \rightarrow EOSO_{4} + H_{2}O$ (7) $E^{0} + H_{2}SO_{4} + 1/2O_{2} \rightarrow EOSO_{4} + H_{2}O$ (7) $E^{0} + H_{2}SO_{4} + 1/2O_{2} \rightarrow EOSO_{4} + H_{2}O$ (7)

Concerning the leaching of metals by direct acid attack; in the absence of an oxidant (air or oxygen), some of the nickel, cobalt and copper from the alloys are believed to be leached by the sulfuric acid according to the reactions 8, 9 and 10. The other possible reactions are the leaching of NiS, FeS, CuS and Cu₂S by the sulphuric acid, reactions (11) through to (14).

$$Ni - Cu + 2H_2SO_4 \rightarrow NiSO_4 + CuSO_4 + 2H_2$$
 (8) $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$ (12) $Ni - Fe + 2H_2SO_4 \rightarrow NiSO_4 + FeSO_4 + 2H_2$ (9) $CuS + H_2SO_4 \rightarrow CuSO_4 + H_2S$ (13) $Ni - Co + 2H_2SO_4 \rightarrow NiSO_4 + CoSO_4 + 2H_2$ (10) $Cu_2S + H_2SO_4 \rightarrow Cu_2SO_4 + H_2S$ (14) $NiS + H_2SO_4 \rightarrow NiSO_4 + H_2S$ (11)

3. Aspen simulation process

Computer simulation is a cost effective means of examining how a process is affected by using certain quantities of chemicals, varying flow rates, or varying operating conditions. Simulating the Ni-Cu matte leaching process on an Aspen Plus simulation package serves as a useful tool to predict the behavior of the process. This simulation acts as a guideline as to how this process will react under actual conditions. Aspen Plus makes it possible to determine the effects of non-ideal conditions on Ni-Cu matte leaching and serves as a guide to the trends that are obtained when analyzing various

sensitivities.

To perform leaching process an autoclave is a basic unit operation, it includes mechanical agitators and the compartments that are separated by weir gates. Basically, the leaching is performed in a compartment where after its content is conveyed into next compartment and so forth. For the present study case, the process model comprises three central unit operations: leaching reactors (autoclave compartments), tank and thickener. Tank was modeled as perfect mixer, whereby the output rate is equal to the sum of the input rates; the tank receives the dissolved metals. Thickeners were modeled as perfect splitters; it mixes all its feed streams then splits the resulting mixture into two or more streams according to substream specifications. Two unit operation models are used to model the leaching reactor: stoichiometric reactor model for carrying out the reactions and splitter model to separate the minerals no dissolved from the dissolved minerals. Within the leaching reactor the equilibrium data and the kinetics are not known, the atomic and mass balances are specified; the operating conditions are 90°C and 1 atm. Here one compartment of the autoclave is simulated as a leaching reactor and a series of simulated compartments stands or a series of leaching reactor.

4. Results and discussion

The figure below illustrates the Aspen simulation flow sheet of Ni-Cu leaching process. The matte feed stream enters at a flow rate of 20 kg/h while 39.2 kg of sulfuric acid in 40 liters of solution enters per hour. The blocks B11, B21 and B31 are the leaching reactors. To model an autoclave of three compartments, three leaching reactors are arranged in series. The output of the block B11 is conveyed into block B21 for further leaching through stream S2; the last leaching reactor, it is fed through stream S5. Streams S3, S6, and S9 are the vents of the gas formed during leaching process. Stream S11 (mineral dissolved) is conveyed into the tank prior further processing of recovering dissolved minerals. To gain a deep insight in the operation and effect of changes in operating conditions, sensitivity analyses were performed.

Leaching rate of the matte - From simulation results, different degrees of extraction among the components of the feed matte are noticed, nickel extraction was the highest followed by that of copper. Generally, according to simulation results, the sulfides are leached to a high extent than their respective metals. The most suitable leaching conditions are as follows: 39.2 kg of sulfuric acid in 40 liters of solution, and reaction temperature ranging from 70 to 80°C. All minerals in the matte are leached to different extents; for each component of matte as a standalone, 32.73% of metallic nickel, 68.64% of nickel sulfide, 5.25% of metallic iron, 12.3% of iron sulfide (pyrrhotite), 7.333% of Pyrite, 12.5% of metallic copper, 18.62 of copper sulfide, 18.25 of chalcocite, 7.833% of metallic cobalt and 2.50% of metallic zinc can be extracted through an autoclave of three compartments under the aforementioned operating temperature and acid concentration.

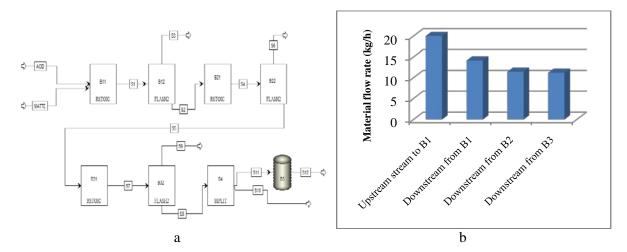


Figure 1. (a) Aspen simulation flowsheet, (b) Matte extraction through the leaching reactors 화학공학의 이론과 응용 제19권 제2호 2013년

5. Conclusions

In this study we have performed a simulation of Ni-Co matte leaching process, the effects of sulfuric acid concentration and temperature on the nickel extraction efficiency are remarkable. Through simulation, the temperature effect on the extraction yields of iron and other components of the feed matte except nickel and copper are proven to be mild. The effects of stirring speed and particle size have not been investigated. Extraction efficiencies of nickel and other minerals in the matte are improved by increasing sulfuric acid concentration. The optimal values of acid concentration and temperature are 39.2 kg of sulfuric acid in 40 liters of solution and 75°C, respectively. Considering the components of matte based on element, 60.35% of nickel, 9.4% of iron, 17.02% of copper, 7.80% of cobalt and 2.5% of zinc can be extracted under suitable conditions of sulfuric acid concentration and reaction temperature.

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References

- [1] S. Yong-feng, X. Wen-ying, L. Wei, "Selective recovery of nickel and cobalt from cobalt-enriched Ni-Cu matte by two-stage counter-current leaching," *Separation and Purification Technology*, 2008, 60(2): 113–119.
- [2] P. H. Kuck, "Mineral Commodity Summaries 2012: Nickel," *United States Geological Survey*, January 2012.
- [3] M. Marafi, A. Stanislaus, "Spent hydroprocessing catalyst management: A review. Part II. Advances in metal recovery and safe disposal methods," *Resources, Conservation and Recycling*, 2008, 53(1/2) 1-26.
- [4] L. Carla, M. Pasquali, "Electrolytic nickel recovery from lithium-ion batteries," *Minerals Engineering*, 2003, 16(6) 537-542.
- [5] C. Lupi, M. Pasquali, A. Dellera, "Nickel and cobalt recycling from lithium-ion batteries by electrochemical processes," *Waste Management*, 2005, 25(2): 215-220.
- [6] J. M. Zhuang, T. Walsh, E. Hobenshield, "Nickel recovery and stabilization of nickel waste tailings," *International Journal of Mining, Reclamation and Environment*, 2006, 20(2): 127–141.
- [7] M. Valix, F. Usai, R. Malik, "Fungal bioleaching of low grade lateritic ores," *Minerals engineering*, 14, No. 2, p. 197 (2001).
- [8] V. Davidson, "Nickel Market Overview The Supply Response," NSG Meeting, CRU Special Steels & Alloys Team (2006).
- [9] U.S. Geological Survey, Mineral Commodity Summaries, January 24, 2012, Virginia.
- [10] S. Stopic, B. Friedrich, N. Anastasijevic, "Kinetics of high pressure leaching of nickel lateritic ore," Pressure hydrometallurgy 2004, 34th Annual Hydrometallurgy Meeting, Canada.
- [11] R. M. Lamya, L. Lorenzen, "Atmospheric acid leaching of nickel-copper matte from Impala Platinum Refineries," *Journal of the Southern African Institute of Mining and Metallurgy*, 2006, 106(6): 385-395.
- [12] J. E. Dutrizac, T. T. Chen, "A mineralogical study of the phases formed during the CuSO₄-H₂SO₄-O₂ leaching of nickel-copper matte," *Canadian Metallurgical Quarterly*, 1987, 26(4): 265–276
- [13] J. A. M. Rademan, L. Lorenzen, J. S. J. van Deventer, "The leaching characteristics of Ni-Cu matte in the acid-oxygen pressure leach process at Impala Platinum," *Hydrometallurgy*, 1999, 52(3) 231–252.
- [14] Z. Hofirek and D. G. E. Kerfoot, "The chemistry of the nickel-copper matte leach and its application to process control and optimization," *Hydrometallurgy*, 29, 1992. pp. 357-381.