RESEARCH PAPER

HYDROMETALLURGICAL NICKEL AND COBALT PRODUCTION FROM LATERITIC ORES: OPTIMIZATION AND COMPARISON OF ATMOSPHERIC PRESSURE LEACHING AND PUG-ROAST-LEACHING PROCESSES

Ozan Coban[1,4], Serkan Baslayici[2,4]*, Mehmet Bugdayci[2,3], Mahmut Ercan Acma[4]

[1] Metallurgical and Materials Eng. Department, Istanbul Gedik University, 34876, Istanbul, Turkey

[2] Construction Technology Department, Istanbul Medipol University Vocational School, 34810, Istanbul, Turkey

[3] Chemical Engineering Dept. Yalova University, 77200 Yalova, Turkey

[4] Metallurgical and Materials Eng. Dept., Istanbul Technical University, 34469, Istanbul, Turkey

*Corresponding Author's email: sbaslayici@medipol.edu.tr, Construction Technology Department, Medipol University Vocational School, 34810, Istanbul, Turkey

ABSTRACT

Corresponding to the technological developments, production and consumption of nickel have increased greatly over time due to its unique mechanical and chemical properties. Therefore, the production of nickel will always keep its importance. The availability of laterite ores, which are oxide type ores, is 86% of the nickel reserves on the Earth, and the processes used in the production of nickel from sulphide type ores have negative environmental effects. Therefore, recovery of nickel from lateritic ores has become increasingly important in recent years. In this study, the aim was to determine the optimum parameters of nickel and cobalt production from limonite type lateritic nickel ores, which were taken from Manisa Caldag region of Turkey, using atmospheric pressure sulfuric acid leaching and pug-roast-leach process. When the results obtained in these processes were compared, it was found that the Ni leaching efficiency is nearly 8% higher and iron leaching efficiency (contamination) is nearly 4% lower in the pug-roast-leach process. Furthermore, the pug-roast-leach process was completed in 33% lower time compared to the atmospheric pressure sulfuric acid leaching process.

INTRODUCTION

Mainly, there are two types of nickel-containing ore deposits. These are sulfide type and laterite types. The sulfide type may contain up to 4% nickel, but on average, it contains from 1% to 2% nickel by weight. Sulfide type minerals' availability is about 14% of the total known nickel reserves. Lateritic oxide ores are considered as the main resources of nickel. Recovery of nickel from laterite ores is becoming increasingly important since their availability is 86% of the nickel reserves on the Earth [1-7].

Extraction of nickel from ores with high Ni/Fe ratio and low moisture content is carried out by pyrometallurgical processes. These processes are also used in nickel extraction from ores with high magnesium content. Disadvantages of pyrometallurgical processes such as high-grade ore requirement, metal loss with slag, high energy requirement, SO₂ removal problems and low cobalt recovery rate increase the cost of nickel production [8]–[16]. Also, high amount of hydrocarbon fuels, coal, oil, naphtha and electricity are used in pyrometallurgical processes. It is necessary to consider the percentages of iron, magnesium and silica which control viscosity, electrical conductivity and melting point of the slag. For all the above reasons, hydrometallurgical processes are preferred instead of pyrometallurgical processes [17-20].

In recent years, there have been studies on the recovery of nickel and cobalt from lateritic ores.

The formation of lateritic rocks on the surface of the Earth occurs over a long time period and is effected by temperature changes and rainfall. Laterite formation begins with the chemical and mechanical effects of air, water and heat, as well as the decomposition of minerals containing magnesium, iron, nickel, cobalt and other components to the generate solution. These solutions percolate to the lower zones over time and finally, lateritic nickel ores which are economically feasible for the recovery of nickel are formed. Lateritic nickel ore deposits with 1% to 3% grade are formed by the decomposition of ultramafic rocks, which contain nickel and cobalt between 0.1% to 0.3%. The decomposition of ultramafic rocks occurs due to atmospheric and hydrospheric phenomena [21–28].

Extraction of nickel from nontronitic or limonitic laterites which have a low Ni/Fe ratio is possible through hydrometallurgical processes. In these processes, leaching of nickel by mineral and/or organic acids can be utilized. Hydrometallurgical processes that are applied to lateritic ores can be divided into three groups such as high-pressure acid leaching, atmospheric pressure acid leaching and acid pug-roast-leach process. High-pressure acid leaching has advantages like; obtaining high metal recoveries (95% for Ni and Co) from limonitic laterites; and eliminating high energy and time-consuming steps such as drying, calcination and reduction. However, high

investment costs due to autoclave lining (titanium lining or acidic brick and lead lining), flash tanks and other expensive equipment are disadvantages of high-pressure acid leaching. Atmospheric pressure acid leaching has advantages such as both providing to utilize saprolitic ores with magnesium content over 6% and also no need for high-cost autoclaves and also high metal recovery. On the other hand, iron is passing to the solution with nickel and cobalt in this process. Contaminants such as Fe, Al, Cr, Mn and Mg, other than nickel and cobalt, are removed by precipitation of these elements and/or separation of nickel and cobalt from the solution to produce nickel and cobalt. Pug-roast-leaching processing can be used as an alternative method for the dissolution of lateritic ore at atmospheric pressure by using sulfuric acid [29–36]. This can be considered as an improved version of the atmospheric pressure sulfuric acid leaching due to the fact that water insoluble oxides are converted to water soluble sulphates. Considering all the above factors, it was decided to use pug-roast-leaching process in the experimental studies in order to see how these processes could be improved and how the disadvantageous sides could be eliminated of atmospheric pressure acid leaching process [27–36].

The aim of this study is to determine the optimum parameters for nickel and cobalt production from limonite type lateritic nickel ores, which were taken from Manisa Caldag region of Turkey, through atmospheric pressure sulfuric acid leaching and pug-roast-leaching processes. An additional aim was to investigate the parameters and the kinetics of the hydroxide precipitation which is carried out after the leaching process.

MATERIAL AND METHODS

In this study, production of nickel and cobalt from limonite type lateritic nickel ores by using hydrometallurgical processes was investigated. In experimental studies, atmospheric pressure sulfuric acid leaching and pug-roast-leaching processes were used to leach nickel from the ore to solution. These processes were applied to milled lateritic nickel ores and leaching efficiencies were compared. Iron removal and mixed hydroxide precipitation processes were applied to pregnant solutions after extraction of the nickel.

Limonite based lateritic nickel ores, which were taken from Manisa Caldag region of Turkey, were used in the experimental studies. Samples of 10 grams of ore were used in each experiment. Chemical analysis of lateritic ore used in the experiments is given in Table 1. The mean grain size of the ore, for which the particle size distribution is shown in Figure 1, was determined to be 27.76 µm. Particle size measurement was carried out with Malvern Mastersizer 2000. Perkin Elmer Aanalyst 800 AAS (Atomic Absorption Spectrometry) was used in chemical analyses for solutions.

**Table 1** AAS results of lateritic ore (wt, %)

Ni	Fe	Co	Cu
1.41	24.94	0.062	0.001
Zn	**Al₂O₃**	**CaO**	**Cr₂O₃**
0.026	4.00	0.66	1.13
K₂O	**MgO**	**MnO**	**Na₂O**
0.25	5.88	0.38	0.08
P₂O₅	**Pb**	**TiO₂**	**SiO₂**
0.03	<0.005	0.13	40.90

Drying of the ore before atmospheric pressure acid leaching and pug-roast-leaching processes was carried out in Thermo Scientific Heraeus drying oven. Leaching experiments were conducted using a magnetic stirrer.
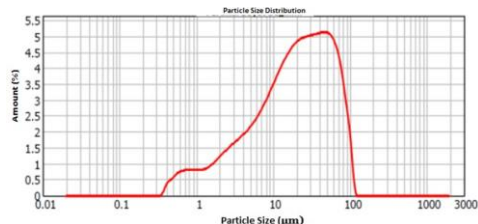
Fig. 1 Particle size distribution of the lateritic ore

The ore was ground in a vibratory cup mill. In the experimental studies, two methods were used to extract the nickel and cobalt from ore. These are atmospheric pressure sulfuric acid leaching and pug-roast-leaching processes. The flowchart for the experimental studies is given in Figure 2.
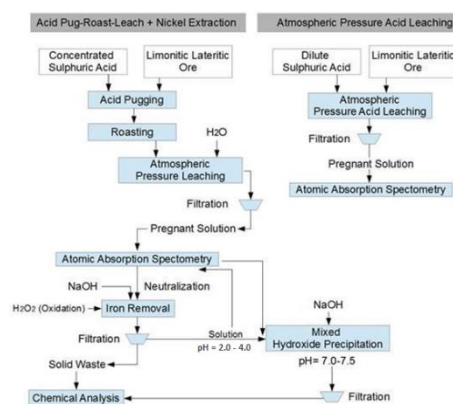

Fig. 2 Flowchart of the experimental studies

Samples of 10 grams of lateritic ore (per experiment), dilute sulfuric acid (H₂SO₄), magnetic stirrer (800 rpm) and filtration system were used in atmospheric pressure acid leaching experiments. Effects of leaching time, acid concentration, leaching temperature, particle size and pulp density on nickel, cobalt and iron leaching efficiencies were investigated. Initially, leaching time experiments were executed. Samples were leached for 30, 60, 90, 120, 150 minutes and the optimum leaching time was determined. Acid concentration experiments were carried out after the optimum leaching time was determined. Samples were leached with sulfuric acid having concentrations of 50, 100, 150, 200 g/l and optimum concentration was determined. Then, the effect of leaching temperature was investigated. Samples were leached at 40, 50, 60, 70, 80, 90°C and the optimum leaching temperature was determined. Particle size experiments were carried out after optimum leaching time, acid concentration and leaching temperature were determined. These optimum parameters were used in the leaching of particles with different average particle sizes. These sizes were 38, 74, 100, 150 and 300 micrometers. Finally, pulp density experiments were carried out by using leaching solutions for 10, 20, 30 and 40% pulp densities in order to determine the optimum pulp density value for atmospheric pressure leaching process.

Samples of 10 grams of lateritic ore, concentrated sulfuric acid (96-98% purity), atmosphere-controlled furnace, magnetic stirrer (800 rpm), distilled water and filtration system were

used in acid pug-roast-water leaching experiments. The effects of acid/ore ratio, roasting time, roasting temperature, leaching duration and pulp density on nickel, cobalt and iron leaching efficiencies were investigated. Theoretical sulfuric acid quantity needed for roasting was calculated as 7 grams of H_2SO_4 per 10 grams of ore according to the chemical analysis of the ore. Acid/ore ratio experiments were carried out with 0.7, 1.0, 1.5, 2.0 grams of acid per 1 gram of ore. After the optimum amount of acid addition was determined, roasting time experiments were executed. Samples were roasted for 30, 60, 90, 120, 150 minutes and the optimum roasting time was determined. Then, the effect of roasting temperature was investigated by roasting the samples at 100, 150, 200, 250 and 300 °C. After the roasting operation, the optimum leaching time was investigated. Samples, which were roasted at optimum conditions, were leached for 30, 60, 90, 120 and 150 minutes by using distilled water. In pulp density experiments, distilled water was used as the solvent and it was added according to the amount of ore used. Pulp densities used in this experiment were 0.10, 0.125, 0.17, 0.25 and 0.50g/ml.

After leaching was performed at optimum conditions in pug-roast-leaching process, iron removal and mixed hydroxide precipitation experiments were performed. For iron removal, oxidation of Fe^{+2} to Fe^{+3} was undertaken using 40 ml of 35% H_2O_2 added to 200 ml of leaching solution with a pH of 1 and stirred with a magnetic stirrer for 15 minutes. Then, the pH of the solution was increased by adding NaOH. The amount of NaOH was calculated stoichiometrically according to Equation 1. It was found that pH value was increased to 4.0 with approximately 40 ml NaOH addition and iron was precipitated as $Fe(OH)_3$. Iron removal efficiencies according to the changing pH values were also investigated.

$$Fe_2(SO_4)_3 + 6NaOH \rightarrow 3Na_2SO_4 + 2Fe(OH)_3 \quad (1.)$$
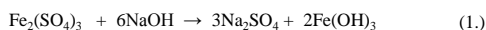
After iron removal was completed, mixed hydroxide precipitation was conducted. The stoichiometric NaOH amount was calculated as 0.15 grams according to Equation 2 and Equation 3. The pH of the solution was increased from 4.0 to 7.5 by adding 6 ml of 3.33M NaOH and stirring with a magnetic stirrer. Nickel and cobalt were precipitated as hydroxides according to Equation 2 and Equation3.

$$NiSO_4 + 2 NaOH \rightarrow Na_2SO_4 + Ni(OH)_2 \quad (2.)$$

$$CoSO_4 + 2NaOH \rightarrow Na_2SO_4 + Co(OH)_2 \quad (3.)$$
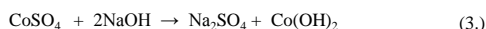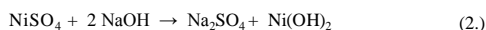
RESULTS AND DISCUSSIONS

In this study, optimum parameters for nickel and cobalt production from limonitic type lateritic ores by using atmospheric pressure sulfuric acid leaching process and pug- roast-leaching process were investigated.
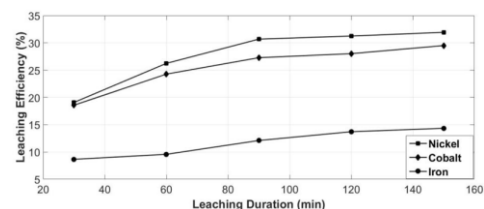

Fig. 3 Effect of leaching time on leaching efficiencies

In the atmospheric pressure sulfuric acid leaching experiments, the effects of leaching time, leaching temperature, acid concentration, particle size and pulp density on the leaching efficiencies were investigated. The effects of leaching time on nickel (Ni), cobalt (Co) and iron (Fe) leaching efficiencies are given in Figure 3. Significant increases in leaching efficiency were observed until leaching time reached 90 minutes. Further increase in leaching time had only a minor effect on leaching efficiencies. Therefore, 90 minutes was chosen as the optimum leaching time.

The effects of acid concentration on nickel (Ni), cobalt (Co) and iron (Fe) leaching efficiencies are given in Figure 4. Nickel, cobalt and iron leaching efficiencies were significantly increased until the acid concentration increased to 150 g/l. When acid concentration increased up to 200 g/l, increase in leaching efficiencies of nickel and cobalt slowed down. On the other hand, leaching efficiency of iron increased significantly. Since iron is not desired in the solution and higher iron causes higher cost of chemicals used for neutralization and precipitation processes, 150 g/l was determined as the optimum acid concentration.
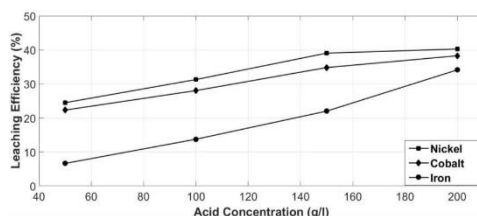

Fig. 4 Effect of acid concentration on leaching efficiencies

Figure 5 show the effect of leaching temperature on nickel (Ni), cobalt (Co) and iron (Fe) leaching efficiencies. As it can be seen on Figure 5, leaching efficiencies for nickel, cobalt and iron increased significantly with increasing leaching temperature until 80°C. When leaching temperature rised above 80°C, leaching efficiency of iron showed an almost linear increase, but increase in the leaching efficiencies of nickel and cobalt slowed down. For this reason, 80°C was determined as optimum leaching temperature.
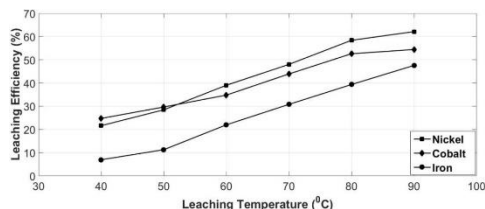

Fig. 5 Effect of leaching temperature on leaching efficiencies

Figure 6 illustrates the effect of particle size on nickel (Ni), cobalt (Co) and iron (Fe) leaching efficiencies. The reaction interface was increased with decreasing particle size and this resulted in higher leaching efficiencies. The increase in leaching efficiencies was not the same for three metals. As can be seen from Figure 6, cobalt leaching efficiency increased significantly when particle size decreased from 100 μm to 74 μm. This result shows that, among these three metals, kinetics is more important in cobalt leaching. Kinetic limitations can be reduced by decreasing the grain size in cobalt leaching. The main targeted metal nickel's leaching efficiencies were not significantly affected by grain size falling below 74 μm. Therefore, the optimum grain size was determined as 74 μm.
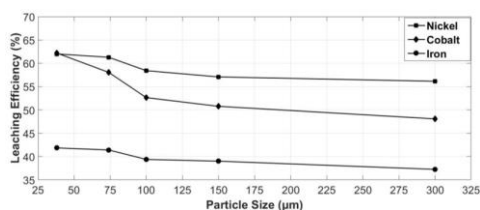
Fig. 6 Effect of particle size on leaching efficiencies

The effect of pulp density on leaching efficiencies was investigated for various acid and water ratios. As it can be seen in Figure 7, leaching efficiencies decreased when pulp density exceeded 10 %. Figure 7 also illustrates that nickel leaching efficiency decreased significantly when pulp density increased from 10 % to 20 % for 150 g/l acid concentration, which was determined as the optimum acid concentration. Since nickel is the main target metal, the optimum pulp density was determined as 10 %.
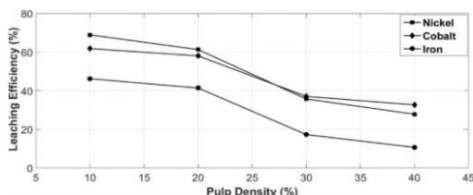

Fig. 7 Effect of pulp density on leaching efficiencies for 150 g/l acid concentration

In the pug-roast-leaching experiments, the effects of acid concentration, roasting time, roasting temperature, pulp density and leaching time (applied after roasting) on leaching efficiencies were investigated. In the acid concentration experiments, the required amount of H_2SO_4 was calculated stoichiometrically based on the quantitative analysis of the ore. 0.7-1.0-1.5-2.0 acid (g)/ore (g) ratios were used in acid concentration experiments. Results are given in Figure 8. Acid concentration is considered as the most important parameter affecting roasting, and hence it also affects leaching efficiency. Theoretically, using sulfuric acid at a weight equivalent to 70 % by weight of the ore is enough for roasting. However, the results of the experiments showed that using sulfuric acid in an amount equal to 150 % of the ore weight is essential for transferring nickel and cobalt to solution. When the acid/ore ratio exceeded 1.5, there was no significant increase in the leaching efficiencies of nickel and cobalt, but there was an important increase in the leaching efficiency of iron. For this reason, the optimum acid/ore ratio was determined as 1.5. Also, it can be seen in Figure 8 that the increase in the acid/ore ratio affects the sulfation and transfer of the iron to the solution more than nickel and cobalt.
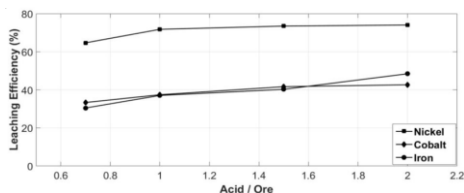

Fig. 8 Effect of acid concentration on leaching efficiencies in pugging process

After determining the optimum sulfuric acid quantity, the effect of roasting time on leaching efficiencies was investigated. Figure 9 shows the effect of roasting time on nickel (Ni), iron (Fe) and cobalt (Co) leaching efficiencies. The increase of roasting time had a slightly positive effect on nickel and cobalt leaching efficiencies. Dissolution of these metals was inhibited because of kinetic reasons. The amount of these two metals in the lateritic ore is relatively low and they show fine distribution within the ore. On the other hand, iron leaching efficiency was not affected by the increase in roasting time. As can be seen in Figure 9, there was no increase in leaching efficiencies for roasting times exceeding 30 minutes. So, 30 minutes was determined as optimum roasting time.
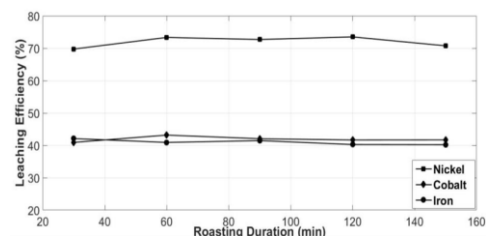

Fig. 9 Effect of sulfation roasting time on leaching efficiencies

After determining the optimum acid concentration and roasting time, the optimum roasting temperature was investigated. Figure 10 shows the effect of roasting temperature on leaching efficiencies of nickel, iron and cobalt. Leaching efficiencies increased with rising roasting temperature. It is known that 575°C is the decomposition temperature of iron sulfates and 675°C is the decomposition temperature of the nickel sulfates [19]. However, even if these temperatures are not reached, it has been seen in the previous studies that sulfates begin to decompose after 450°C, therefore leaching efficiencies start to decrease. Therefore, temperatures over 300°C were not used in the experiments and 300°C was determined as the optimum roasting temperature.
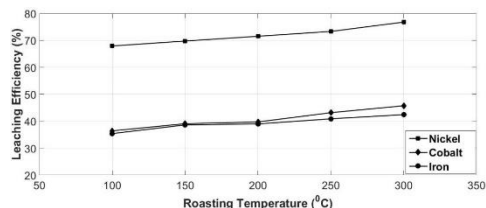

Fig. 10 Effect of sulfation roasting temperature on leaching efficiencies

After sulfation roasting was carried out with optimum conditions, the effect of leaching time on leaching efficiencies was investigated. Leaching was executed after roasting, and water was used in this process. Figure 11 shows the effect of leaching time on the leaching efficiencies of nickel, iron and cobalt. Leaching efficiencies increased until leaching time reached 30 minutes. A further increase in leaching time had no significant effect on leaching efficiencies. Therefore, 30 minutes was determined as the optimum leaching time.

After roasting, an intermediate product which consists of mixed sulphates was formed. This intermediate product was weighed, and water was added at various amounts to obtain different pulp densities. Figure 12 shows the effect of pulp density on leaching efficiencies of nickel, iron and cobalt. Leaching efficiencies decreased with increasing pulp density.

Decreases in nickel and cobalt leaching efficiencies were higher when compared to the leaching efficiency of iron. Although maximum leaching efficiencies of nickel and cobalt were achieved at 0.1 g/ml pulp density, optimum pulp density was determined as 0.125 g/ml, because the leaching efficiency of iron was affected more negatively with the increase in pulp density when compared to cobalt and nickel.
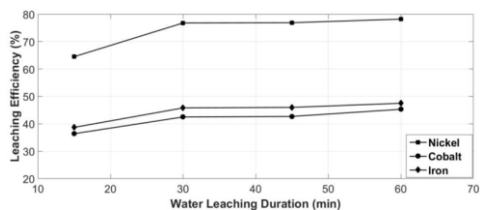

Fig. 11 Effect of leaching time on leaching efficiencies
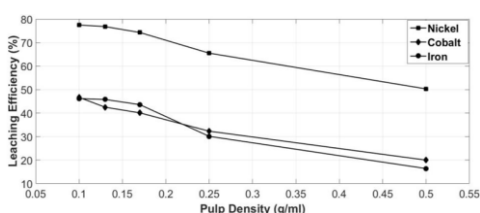

Fig. 12 Effect of pulp density on leaching efficiencies

Leaching efficiencies obtained in the two processes for optimum conditions were compared and it was found that nickel leaching efficiency was higher and iron leaching efficiency was lower for the pug-roast-leaching process as indicated on Figure 13. Therefore, iron removal and mixed hydroxide precipitation processes were applied to the samples subjected to the pug-roast-leaching process.
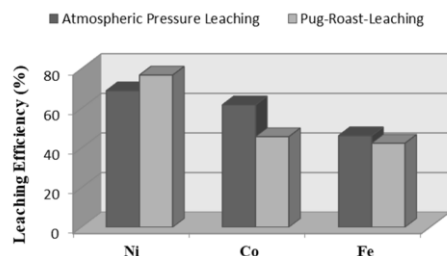

Fig. 13 Comparison of Processes for Leaching Efficiencies

After the pug-roast-leaching process was carried out at optimum conditions, iron removal was applied to the solution. The efficiency of this process was measured using AAS analysis. After this process was completed, nickel and cobalt were precipitated by mixed hydroxide precipitation process. The efficiency of the mixed hydroxide precipitation was calculated from AAS analysis data.

In the iron removal process, 40 ml of H_2O_2 was added drop by drop to 200 ml of pregnant solution for oxidation. Then, 3.33M NaOH was added to this mixture and it was observed that iron in the solution was precipitated. During this process, the effect of pH value on iron removal efficiencies and also nickel loss were investigated. Solid and liquid phases were separated by using filtration. When the AAS analysis which was performed after the iron removal process and the AAS analysis which was

performed before the iron removal process were compared, it was found that 98.6% of iron was precipitated on pH value 4.0 as indicated on Figure 14. However, it was seen that 17.2% of the nickel was lost together with the precipitate in the iron removal process. As it can be seen on Figure 14, nickel loss percentage increases over 3.5 pH value while iron removal efficiency does not significantly. Optimum pH value for iron removal process was determined as 3.5. Nickel partially precipitates together with iron which precipitates as very fine-grained iron hydroxide compound. That would be the reason for the loss of nickel.
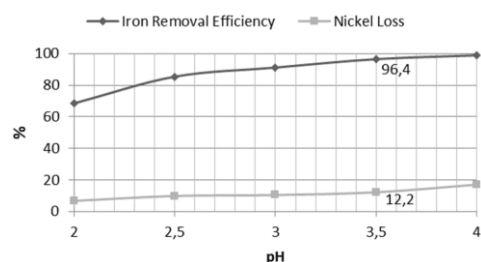

Fig. 14 Effect of pH to Iron Removal Efficiency and Nickel Loss

In the mixed hydroxide precipitation process, initially, the pH of the solution was increased to 7.5 with 8 ml of 3.33M NaOH addition. Solid which contains nickel and cobalt hydroxides and residual iron hydroxide, and liquid which contains a trace amount of manganese, magnesium and residual nickel and cobalt were separated from each other by filtration. Then filter cake was dissolved in 15 ml HCl + 5 ml HNO_3. Afterward, AAS analysis was conducted on the two solutions. According to the results, it was seen that 90.8% of nickel and 75.2% of cobalt were precipitated.

CONCLUSION

In this study, nickel and cobalt were extracted from limonite type lateritic nickel ores, which were taken from Manisa Caldag region of Turkey, by using atmospheric pressure sulfuric acid leaching and pug-roast-leaching processes. In atmospheric pressure sulfuric acid leaching experiments, the effects of leaching time, acid concentration, particle size and pulp density on leaching efficiencies were investigated. According to the results, optimum parameters were determined as; 150 g/l H_2SO_4 concentration, 80°C leaching temperature, 90 minutes of leaching time, 74 µm particle size and 10% pulp density. Leaching efficiencies of 68.9% Ni and 61.8% Co were obtained at optimum conditions. On the other hand, 46.2% of the iron in the ore was dissolved. In pug-roast-leaching experiments, the effects of acid concentration, roasting temperature, roasting time, pulp density and leaching time (applied after roasting) on leaching efficiencies were investigated. Optimum conditions were determined to be: 1.5 acid (H_2SO_4)/ore ratio, 300°C roasting temperature, 30 minutes of roasting time, 0.125 g/l pulp density and 30 minutes of leaching time. Leaching efficiencies of 76.8% Ni, 45.7% Co and 42.4% Fe were obtained with optimum parameters. When atmospheric pressure sulfuric acid leaching and pug-roast-leaching processes were compared, it was seen that Ni leaching efficiency was nearly 8% higher and iron leaching efficiency was nearly 4% lower in pug-roast-leaching process. Lower iron leaching efficiency will result in less neutralization reagent and oxidant used in the iron removal process, and this will reduce operating costs. Moreover, the atmospheric pressure sulfuric acid leach-

ing process is completed in 90 minutes, while the pug-roast-leaching process takes 60 minutes. Shortening the duration by 33% is very important for industrial scale production.

The leaching efficiencies obtained seem to be a little bit low and the main reason for this would be the lack of acid regeneration during leaching. The efficiencies could be increased by returning the acid which contains nickel and cobalt to the beginning of the leaching or pugging processes. If acid conversion and sulfuric acid production are done at the end of the pug-roast leaching process, nickel and cobalt leaching efficiencies would increase and metal loss would be minimized.

According to the results obtained in this study, nickel and cobalt production from limonite type lateritic nickel ores, which were taken from Manisa Caldag region of Turkey can be carried out efficiently by hydrometallurgical processes. When we consider the importance of the materials such as stainless steels, high quality alloyed steels and nickel and cobalt based super alloys, this ore and these methods are significant for the production and industrial scale production can be integrated to the parameters that have been optimized in this study.

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