

HIGH PRESSURE ACID LEACHING OF A TURKISH LATERITE ORE

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ABSTRACT

Worldwide, most of the primary nickel is produced mainly by energy intensive pyrometallurgical routes from sulphide based nickel ores. However, the trend in supplying the world nickel demand is changing towards the hydrometallurgical extraction route from the more abundant (about 70% of the world's land-based nickel resources) laterite type nickel resources. In this study; the fundamental HPAL (High Pressure Acid Leaching) process parameters like leaching temperature, duration, acid/ore ratio, feed size, heat treatment the ore prior to the leaching process, effect of Na_2SO_4 , and FeSO_4 additions on nickel and cobalt extractions from the Western-Anatolian, Manisa/Gördes lateritic nickel ore were studied and the economically optimum values have been determined as process parameters for this lateritic nickel reserve.

Keywords: Extractive metallurgy, Hydrometallurgy, Leaching, Oxide ores,

1. INTRODUCTION

Nickel laterite deposits are formed by intense weathering of ultramafic rocks, such as peridotites and serpentinites exposed to tropical to sub-tropical climates. These deposits account for approximately 40-45% of annual nickel production globally and contain about 70% of the world's total land-based nickel resources. Due to the weathering effect of localized rainfalls,

biological activity on the top soil, and temperature-pressure variations in the ultramafic region, minerals in the bedrock dissolve in different rates depending on their solubility and then re-precipitate or form solid solutions within the crystal lattice of some minerals [1]. Thereby, comparatively different dissolution and re-precipitation characteristics, in turn, form different layers in the bedrock as a result of different mineral enrichments so called the lateritic profiles [2].

Depending on the weathering history, typically a layer of mainly ferrous or siliceous gangues may exist on top of the laterite profile. Under this layer, poorly nickel containing hematite dominant layer may exist. Following, goethite dominant, hematite, and silica containing so called limonitic layer takes place in the reserve. In some lateritic formations possibly a transition nontronitic laterite profile takes place between the upper limonitic and lower saprolitic layers. Nontronite is an iron rich clay mineral and nickel is distributed within the crystal lattice of this mineral. Finally, saprolite layer is dominated by nickel rich hydrous magnesium silicates in which nickel is primarily in the crystal lattice of the mineral serpentine [3].

Contemporary nickel laterite formation is confined to low latitudes where temperature, rainfall, and consequently groundwater through-flow are high. Laterites located at higher latitudes and with cooler climatic regimes (e.g. Turkey, Greece, and Macedonia in Balkan Region) are considered to be paleodeposits which originally formed at lower latitudes during warmer climates. In recent years, the exploration for nickel laterites in Turkey has resulted in the discovery of three important laterite deposits namely; Manisa/Gördes, Çaldağ and Sivrihisar. This research is based on the high pressure acid leaching of Manisa/Gördes lateritic nickel ore.

2. CHARACTERIZATION OF ORE

In this study; limonitic and nontronitic nickel laterite ores of Gördes which have an estimated reserve of 32 million tons on dry basis were studied [4]. Firstly, the representative limonitic and nontronitic laterite samples of Gördes at an as received size of -20 mm were weighed and dried in a drying oven at 105°C, and the moisture contents of the ores were determined as given in Table 1.

Table 1. Moisture contents of the lateritic ores

	Moisture Content, % w/w	Mass Received, kg
Limonitic Ore	23.5	200
Nontronitic Ore	40.1	410

After the moisture content determinations, the nontronitic ore was ground to a size of -850 μ , and the limonitic sample was ground to various sizes, such as -2.0 mm, -1.4 mm, -850 μ , -425 μ , and -38 μ , respectively, in order to study the effect of feed size on nickel and cobalt extractions in the pressure acid leaching experiments in an autoclave.

Both bulk and solid density measurements were conducted for each lateritic sample, and the results obtained are given in Table 2. Bulk density measurements were done for both as received laterite ore samples (-20 mm) and calculated according to the ratio of ore weight to ore volume without joggle. A helium pycnometer was used to determine the solid density of the finely ground (-38 μ) limonitic and nontronitic ore samples.

The chemical analyses of Gördes limonitic and nontronitic nickel laterites are given in Tables 3 and 4, respectively.

Table 2. Bulk and solid densities of lateritic samples (gm/cm³)

	Limonite	Nontronite
Bulk Density, Wet ore	1.04	0.93
Solid Density	3.26	2.64

Table 3. Chemical analysis of Gördes limonite ore (%)

Limonite	Fe	Ni	Co	Cr ₂ O ₃	MnO	As	Al ₂ O ₃	SiO ₂	P ₂ O ₅	MgO	CaO	TiO ₂	CuO
ICP Data	28.80	1.10	0.083	1.99	0.59	0.68	5.83	28.8	0.02	2.26	1.27	0.13	0.039

Table 4. Chemical analysis of Gördes nontronite ore (%)

Nontronite	Fe	Ni	Co	Cr ₂ O ₃	MnO	As	Al ₂ O ₃	SiO ₂	P ₂ O ₅	MgO	CaO	TiO ₂	CuO
ICP Data	15.95	1.20	0.044	0.99	0.34	0.02	4.17	44.9	0.05	6.91	2.15	0.08	0.009

As concluded by a similar study of Gleeson et al [5], the chemical analysis conducted by ICP (Inductively Coupled Plasma) verified that the limonitic sample contained relatively high iron, cobalt, chromium oxide (Cr₂O₃) and arsenic, whereas the nontronitic sample contained higher Ni, MgO, SiO₂ and CaO as compared to the limonitic laterite ore.

After obtaining the chemical analysis results, samples were subjected to XRD (X-Ray Diffraction) analysis in order to characterize the type of minerals present in these laterite samples. For X-Ray diffraction analysis a Rigaku D/MAX2200/PC Model diffractometer with Cu-K α tube working under 40 kV and 40 mA was used.

By combining the chemical analysis and XRD analysis results for the limonitic sample, it was found that the limonitic sample contained high amounts of quartz (SiO₂), hematite (Fe₂O₃), and goethite (FeOOH) as well as the mineral smectite (Na_{0.3}Fe₂(Si,Al)₄O₁₀(OH)₂.nH₂O) as seen in Figure 1.

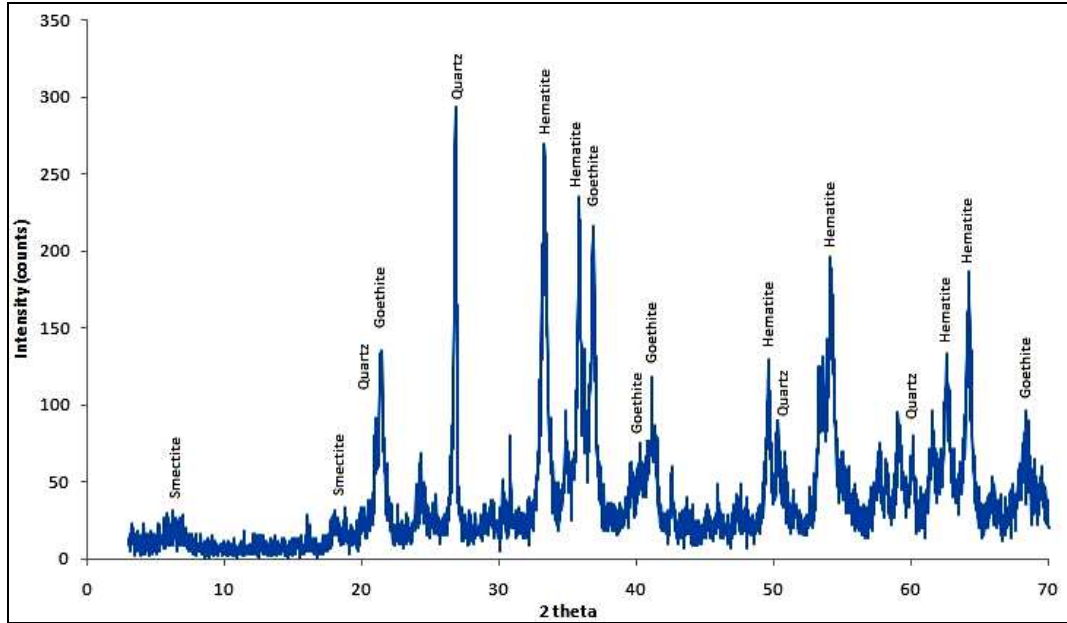


Figure 1. XRD pattern of the limonitic sample

The same procedure for nontronitic sample has indicated that this sample was consisted high amounts of the mineral serpentine ($(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$), quartz (SiO_2), goethite (FeOOH) and smectite ($\text{Na}_{0.3}\text{Fe}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$) as well as calcite (CaCO_3), as shown in Figure 2. SEM (Scanning Electron Microscopy) studies on both samples by the help of Nova Nanosem 430 indicated that nickel was mainly present in the crystal lattices of the minerals goethite (FeOOH), hematite (Fe_2O_3), serpentine ($(\text{Mg, Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$) and smectite ($\text{Na}_{0.3}\text{Fe}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$). On the other hand, cobalt was mainly present in the crystal structure of the mineral asbolane $(\text{Co,Ni})_{1-y}(\text{Mn}^{4+}\text{O}_2)_{2-x}(\text{OH})_{2-2y+2x} \cdot \text{H}_2\text{O}$ [6].

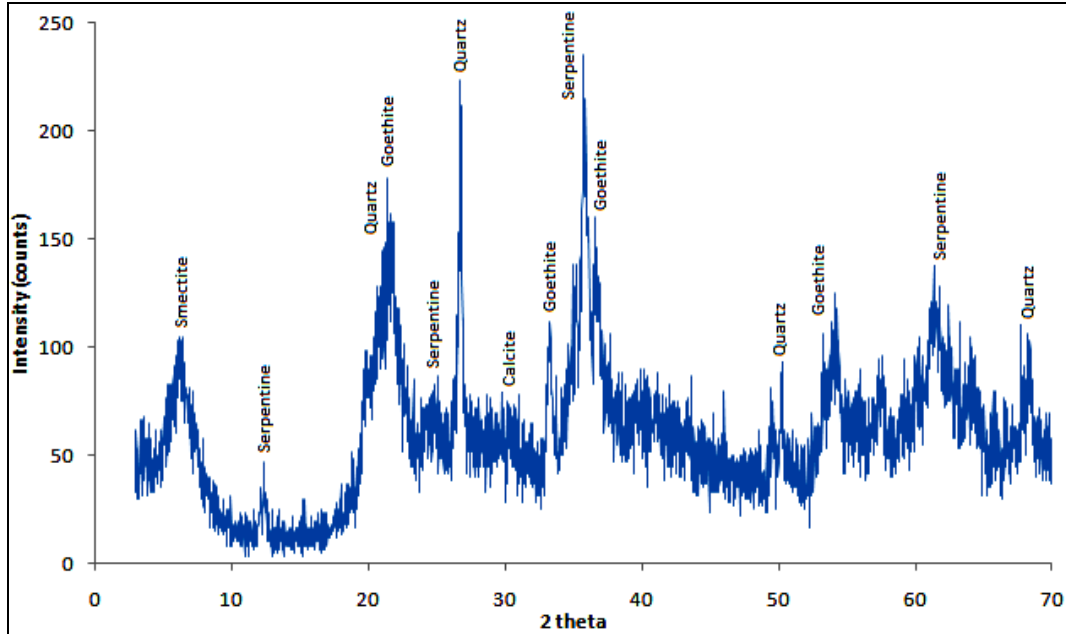


Figure 2. XRD pattern of the nontronitic sample

3. EXPERIMENTAL PROCEDURE

For high pressure acid leaching tests Parr-4532 model, 2 liter, titanium grade-4 autoclave having automatic heating and cooling unit, and magnetically driven stirrer was used as leaching apparatus.

According to the results of a study on the effect of ore type done by Whittington et al. [7], it was shown that the leachability of nontronitic type laterites is better than the limonitic ones which was also observed and confirmed with the Gördes laterites, and in this study the leaching tests were decided to be performed only with the difficult to leach limonitic laterite sample. For this purpose, the limonitic ore was slurried with pre-determined amount of de-ionized water and after the addition of necessary amount of sulphuric acid (95-98 wt %) and other reagent grade additives when necessary, the reactor was closed and the automatic heating unit was adjusted to

the desired set-point. The start of the reaction defined as zero time was determined when the reactor temperature reached to the set point and then the reaction was let to proceed until the target leaching duration was attained.

After the leaching process was terminated, the reactor was allowed to cool down to room temperature approximately in 1 hour by means of water flowing through a titanium cooling coil, then the resultant slurry was filtered by the aid of an acid resistant vacuum pump and Whatman grade-40 filter paper placed on a Buchner funnel in order to separate the pregnant leach solution (PLS) loaded with metal ions from the leach residue. While the pregnant leach liquor was taken for residual free acid determination, ORP, and density measurements; chemical analyses were also conducted by AAS (Atomic Absorption Spectroscopy) method for nickel, cobalt, iron, aluminum, manganese, chromium and magnesium. For residual acid measurements, potassium oxalate solution was used as a complexing media for titration in which the free acid in the pregnant liquor solution was titrated with NaOH, and the corresponding amount of free acid was determined. For ORP measurements, a Pt/Ag-AgCl electrode (saturated with KCl) was used throughout the experimental studies. The resultant solid leach residue was taken after washing with a slightly acid solution and dried in a laboratory oven for nearly 12 hours before XRF (X-Ray Fluorescence) analysis. Then, the metal extraction calculations were performed from the solid and PLS analysis data.

Before investigating the pressure acid leaching process parameters, successive three tests were performed under the same conditions in order to see whether the experimental procedure and the metal extraction results obtained were reproducible or not. According to the results obtained from the HPAL reproducibility tests, the standard deviation of the mentioned three experiments

was 0.58% for nickel and 1.76% for cobalt extraction values. Therefore, the experimental results were considered to be reproducible.

4. EXPERIMENTAL PARAMETERS STUDIED

4.1. Effect of Leaching Temperature

In order to see the effect of leaching temperature on the degree of nickel and cobalt extractions, the following tests were conducted between the temperature range of 245°C and 270°C with the following process parameters; 30% solids, 300 kg acid/ton dry ore, 1 hour leaching duration, and minus 850 μ particle size. According to the experimental results given in Figure 3, the degree of nickel extraction increased linearly up to 255°C, then the increasing trend decreased slowly, and finally ceased between 265-270°C. Nearly the same trend has been observed in the extraction of cobalt as a result of temperature rise within the afore-mentioned temperature range. In contrast to Ni and Co; the aluminum extraction tended to decrease as a result of increase in Al precipitation rate and inverse solubility of alunite as stated by Whittington and Muir [3]. Similarly, the chromium extraction tended to decrease as a result of increase in leaching temperature, however, it was not as obvious as the decrease in the degree of extraction observed in the case of aluminum. By considering the experimental findings and taking the industrial HPAL processes into account, the leaching temperature was chosen as 255°C for the rest of the experiments in order to optimize the other process parameters. Since, higher operating temperature means higher energy consumption especially in the form of steam for heating and maintaining the autoclave at a high temperature together with higher initial equipment costs, the desired nickel and cobalt

extractions were intended to be reached with the lowest possible and most widely industrially used leaching temperature.

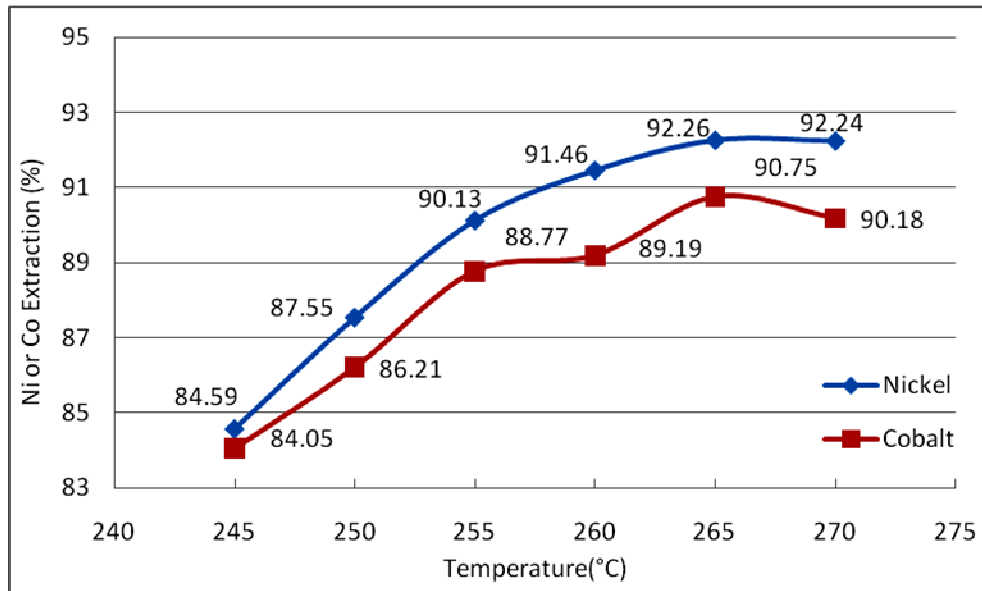


Figure 3. Effect of leaching temperature on nickel and cobalt extractions

(Particle size: 100% -850 μ with 300 kg sulphuric acid addition per ton of dry ore at 30% solids
for one hour leaching duration)

4.2. Effect of Leaching Duration

In order to see the effect of increasing leaching duration on nickel and cobalt extractions under the previously chosen constant conditions, successive five tests were conducted. It was found that the nickel and cobalt extractions increased almost linearly up to about 90 minutes of leaching duration and then tended to stabilize between the leaching durations of 90 and 360 minutes as seen in Figure 4. As the leaching duration was prolonged, the extractions of Al, Fe and Cr were affected negatively possibly due to the increase in the precipitation of these ions from PLS. This finding was also verified with the increase in the amount of residual free acid as

a result of longer leaching durations. According to the experimental results, the amount of residual free acid increased linearly from nearly 40 to 46 gpl over time meaning that Al, Fe, and Cr tended to precipitate and gave up the bounded acid within the metal sulphates in progress of time. Moreover, the leaching tests indicated that most of the Mn and Mg present in limonitic laterite ore of Gördes readily dissolved in sulphuric acid solution under pressure and their concentrations should be controlled in order to aid the following down-stream solution purification steps. By considering the industrially most widely used 60 minutes of leaching duration at temperature for limonitic nickel laterites in the light of the above findings, 60 minutes of leaching duration was chosen for the rest of the tests in order to optimize other process parameters.

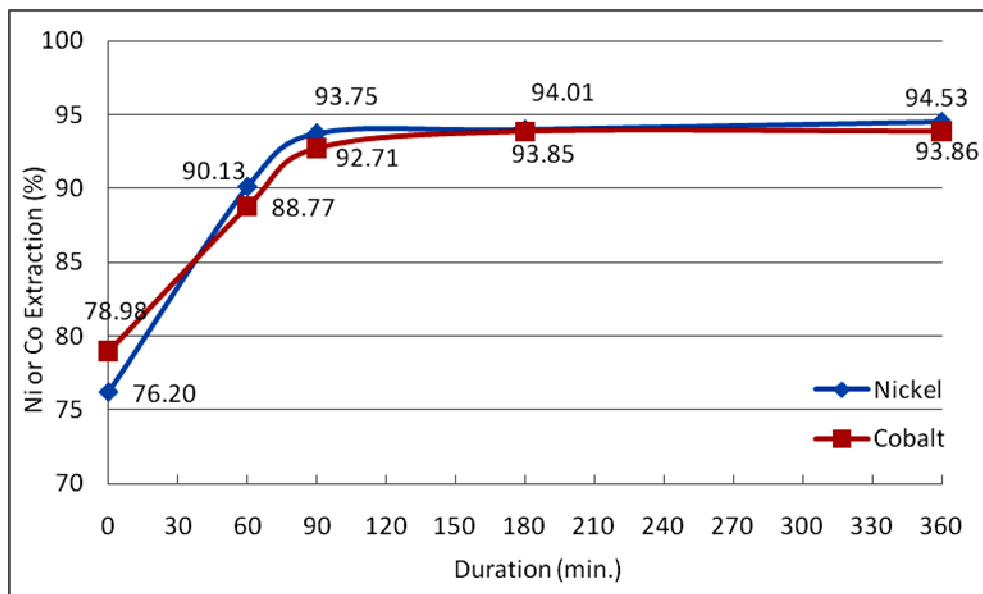


Figure 4. Effect of leaching duration on nickel and cobalt extractions

(Particle size: 100% -850 μ at 255°C leaching temperature with 300 kg sulphuric acid addition per ton of dry ore at 30% solids)

4.3 Effect of Acid Concentration

In order to find the amount of sulphuric acid required to obtain the maximum nickel and cobalt extractions together with the minimum residual free acid in the final liquor, different sulphuric acid additions in the range of 275-350 kg per ton of dry ore were tested under the previously determined constant conditions. The range of acid concentration to be studied was determined after a theoretical stoichiometric calculation based on the Sherritt Formula. From the nickel and cobalt extraction values given in Figure 5 together with the residual free acid measurements, 300 kg of sulphuric acid per ton of dry limonitic ore was found to be enough for the desired extraction values. Since, according to the industrial experience and literature data 30-40 gpl of residual free acid in PLS is enough in order to reach the desired degree of nickel extractions [3]. Therefore, in these experiments nearly 40 gpl of residual acid has been targeted. Acid amount of greater than 300 kg per ton of dry ore was unnecessary since the residual acid increased from nearly 39-40 gpl to 43-45 gpl, and in the next stages of nickel and cobalt recovery from PLS, the resultant excessive residual free acid should be neutralized with a basic reagent (e.g. CaCO_3) which would increase the overall production costs. Additionally, a slight increase in the concentration of iron in the pregnant leach solution resulted in the other experiments to be performed with 300 kg of sulphuric acid per ton of dry limonitic laterite ore.

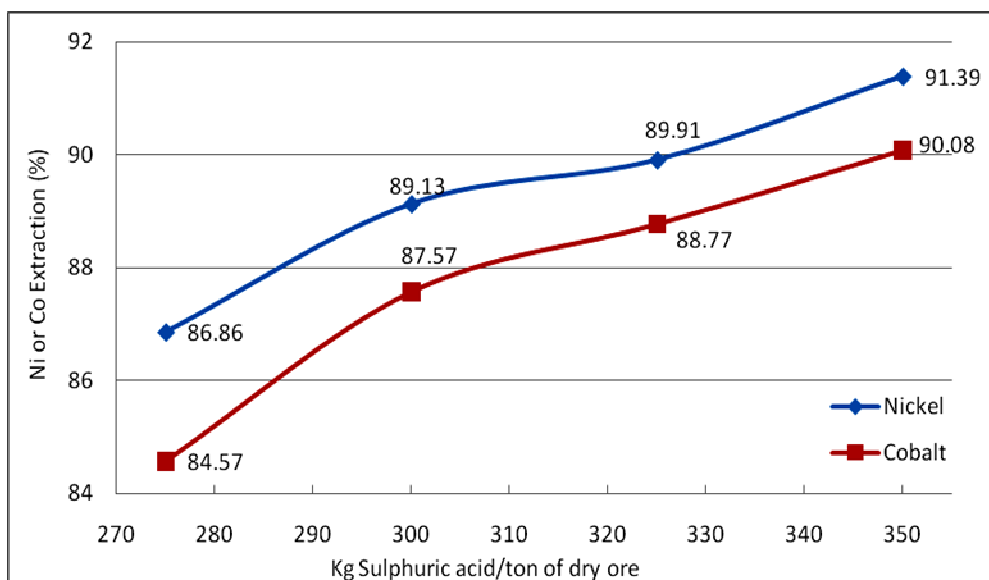


Figure 5. Effect of sulphuric acid concentration on nickel and cobalt extractions

(Particle size: 100% -850 μ at 255°C leaching temperature at 30% solids for one hour leaching duration)

4.4. Effect of Feed Size

According to the data obtained from the leaching tests of the limonitic laterite samples having different particle sizes under the previously determined constant conditions; the cobalt extractions for particle sizes greater than 850 μ , and the nickel extractions for particle sizes greater than 1.4 mm were unsatisfactory. In contrast, for the limonitic ore particle sizes finer than 425 μ , there was a considerable increase in the extraction of cobalt and a slight increase in the extraction of nickel as seen in Figure 6 which shows that excessive grinding seems to be helpful for the extraction of valuable metals. Additionally, a considerable decrease in the extraction of Al, and a slight decrease in the extraction of Fe meant that a desirable decrease in the impurity ratio of the pregnant liquor solution was present. However; since the particle sizes finer than

425 μ makes the ore preparation steps more difficult, time consuming and energy intensive, finer grinding of the ore as a useful option was rejected since it is not commercially attractive. Moreover, intensive filtration problems of the resulting slurry after leaching due to excessive grinding, and a slight increase in the impurity content of Mn in the pregnant leach solution led to the choice of particle size of 100% - 850 μ for the rest of the tests.

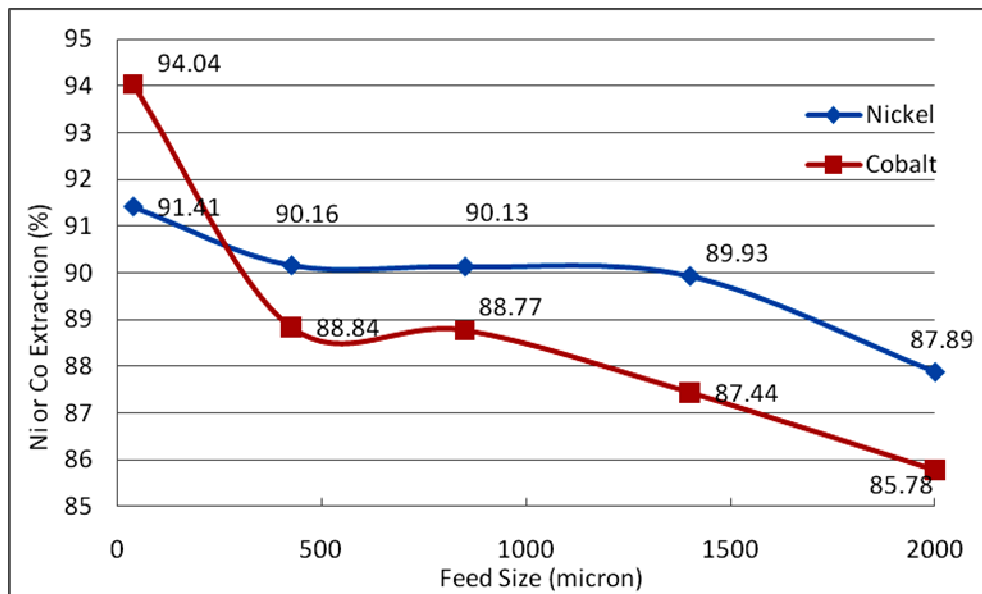


Figure 6. Effect of particle size on nickel and cobalt extractions

(Leaching temperature of 255°C with 300 kg sulphuric acid addition per ton of dry ore at 30 % solids for one hour of leaching duration)

4.5 Effect of Prior Limonitic Laterite Heat Treatment

According to a study published on economic geology [8], the leaching characteristics of goethite is much better than that of hematite which suggests that the nickel leach extractions of limonitic samples with higher hematite contents may be less than those of higher goethite containing ones.

In order to test this argument, Gördes limonitic laterite sample containing both nickel bearing hematite and goethite minerals was heat treated in air at 350°C for 1 hour to fully convert the whole goethite mineral to hematite depending on the obtained DTA/TGA (Differential Thermal Analysis and Thermo Gravimetric Analysis) results of the limonitic sample given in Figure 7.

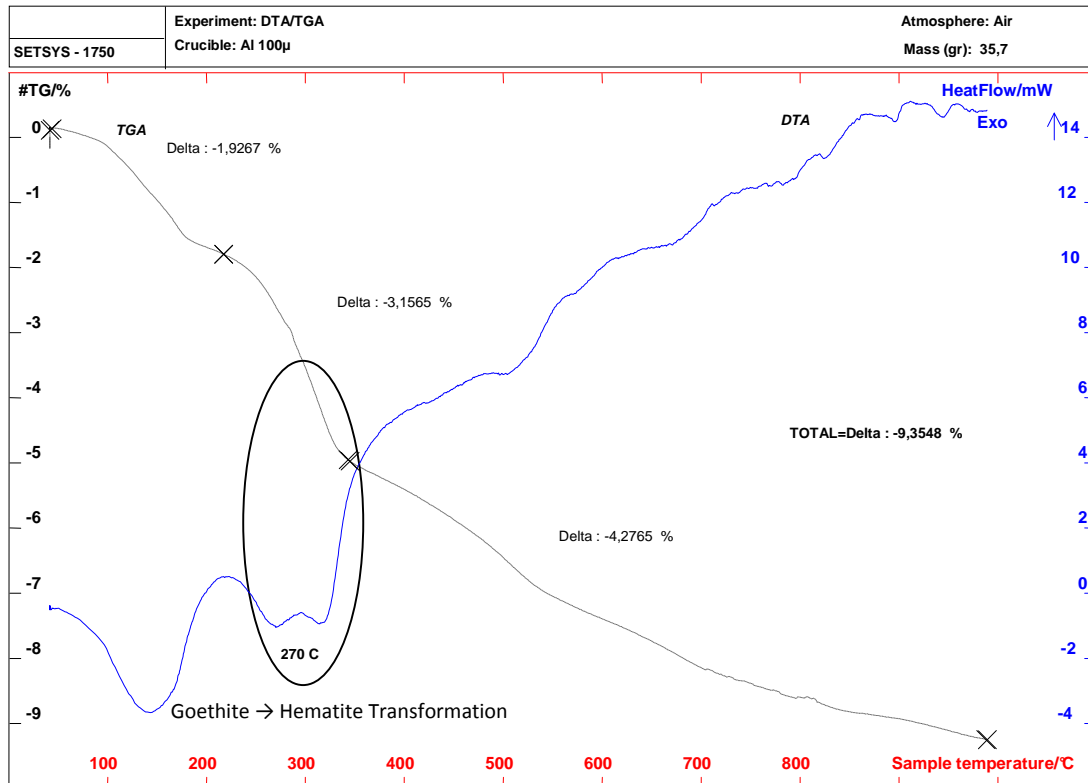


Figure 7. DTA and TGA result of the limonitic sample

After pressure leaching the heat treated limonitic ore sample in the autoclave having a particle size of 100% -850 μ at 255°C, with 300 kg sulphuric acid per ton of dry ore at 30% solids (w/w) for one hour, it was noticed that the nickel and cobalt extractions decreased drastically from 90.13% to 76.35% and from 88.77% to 79.11%, respectively. Thus, it was shown that the presence of relatively high amount of nickel containing hematite mineral within the limonitic

laterite ore sample was responsible for the low nickel and cobalt extractions within one hour of leaching duration the results of which can be seen in Figure 8. Some XRD and SEM studies carried out previously on some of the leach residues also indicated that nickel and cobalt were not fully leached mostly from primary hematite present in the limonitic ore of Gördes under the standard HPAL conditions. Therefore, the following tests were planned in order to overcome this problem originating from refractory hematite mineral as much as possible.

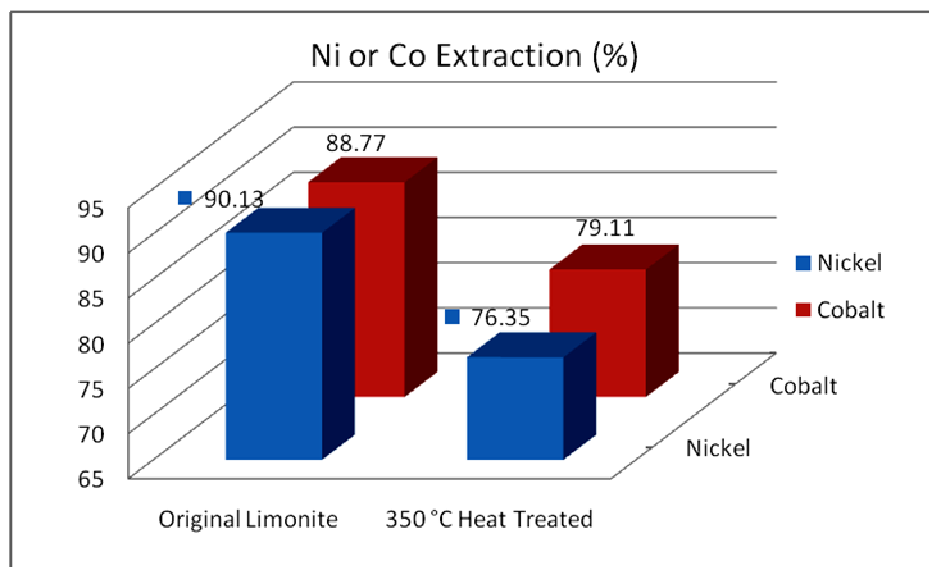


Figure 8. Effect of prior heat treatment on nickel and cobalt extractions

(Particle size: 100% -850 μ at 255°C leaching temperature with 300 kg sulphuric acid addition per ton of dry ore at 30% solids for one hour leaching duration)

4.6. Effect of HCl Addition

In order to see the effect of HCl addition on the nickel and cobalt extractions 5 and 10 grams of HCl (37 wt %), corresponding to 33.33 and 66.67 kgs per ton of dry ore were tested under the previously determined constant conditions, respectively. When HCl was added initially to the

leaching solution together with H_2SO_4 , the nickel and cobalt extractions were affected positively with the increasing amount of HCl addition as seen in Figure 9. Besides nickel and cobalt, there were only a slight increase in the amounts of dissolved iron and chromium in the leach solution due to HCl addition. Finally, there was no considerable and beneficial change in the extractions of other elements after leaching. Despite the beneficial effect of HCl addition upon the nickel and cobalt extractions, further experimental studies with HCl addition were not proceeded due to the corrosive attack of this leaching media which led to undesired failures of the pressure leaching equipment bursting plate. Thus; in short, HCl addition might be an alternative option upon enhancing the nickel and cobalt extractions, if more corrosion resistant autoclave system could be devised in order to endure the side effects of the sulphuric and hydrochloric acid mixtures.

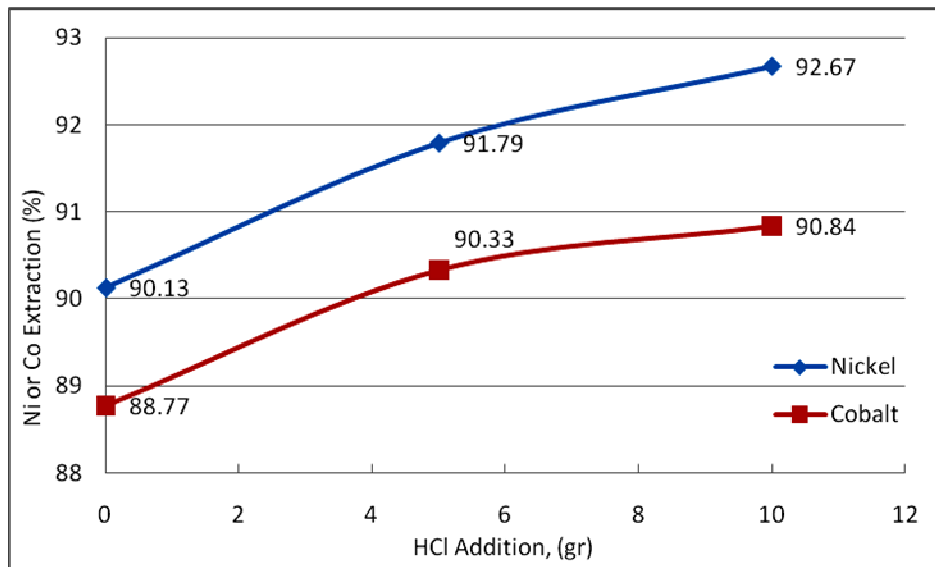


Figure 9. Effect of HCl addition on nickel and cobalt extractions

(Particle size: 100% -850 μ at 255°C leaching temperature with 300 kg sulphuric acid addition per ton of dry ore at 30% solids for one hour of leaching duration)

4.7. Effect of Na₂SO₄ Addition

According to the results obtained from 4.4 grams (12.5 gpl) and 8.8 grams (25 gpl) of Na₂SO₄ addition experiments under the previously determined constant conditions, there was a decrease in nickel extraction values as seen in Figure 10. For cobalt, the results were even more disappointing as compared with nickel. However, although Na₂SO₄ addition was not useful in improving nickel and cobalt yields, it was very effective in controlling the impurity level of the pregnant leach solution. According to the experimental results obtained, extractions of aluminum and chromium into the PLS dropped from 20% to 2% and 2% to 0.3%, respectively. Thus most of the aluminum and chromium were prevented from passing into the liquor. Additionally, there was a decreasing trend in the extraction of magnesium into the pregnant leach solution. However, despite the some positive effects of Na₂SO₄ addition in obtaining cleaner PLS, deterioration of filtration properties of the leach residue led the further studies to be terminated.

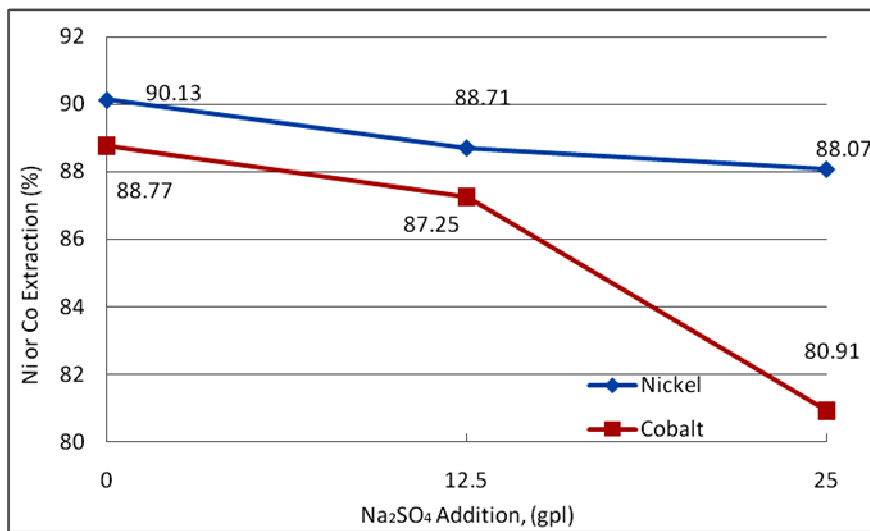


Figure 10. Effect of Na₂SO₄ addition on nickel and cobalt extractions

(Particle size: 100% -850 μ at 255°C leaching temperature with 300 kg sulphuric acid addition per ton of dry ore at 30% solids for one hour of leaching duration)

4.8. Effect of FeSO₄ Addition

In order to see the effect of FeSO₄ addition on nickel and cobalt extractions, 5 grams (14.3 gpl) and 10 grams (28.6 gpl) of FeSO₄ was added into the system under the previously determined constant conditions, respectively. As seen in Figure 11, these increasing additions of FeSO₄ gave somewhat encouraging results as long as only the nickel and cobalt extractions were concerned. However, due to the very time consuming solid/liquid separation problems encountered during filtration and the undesired increase in the dissolved iron cations, especially in the form of ferrous ions in the pregnant leach solution, further tests were decided to be ended.

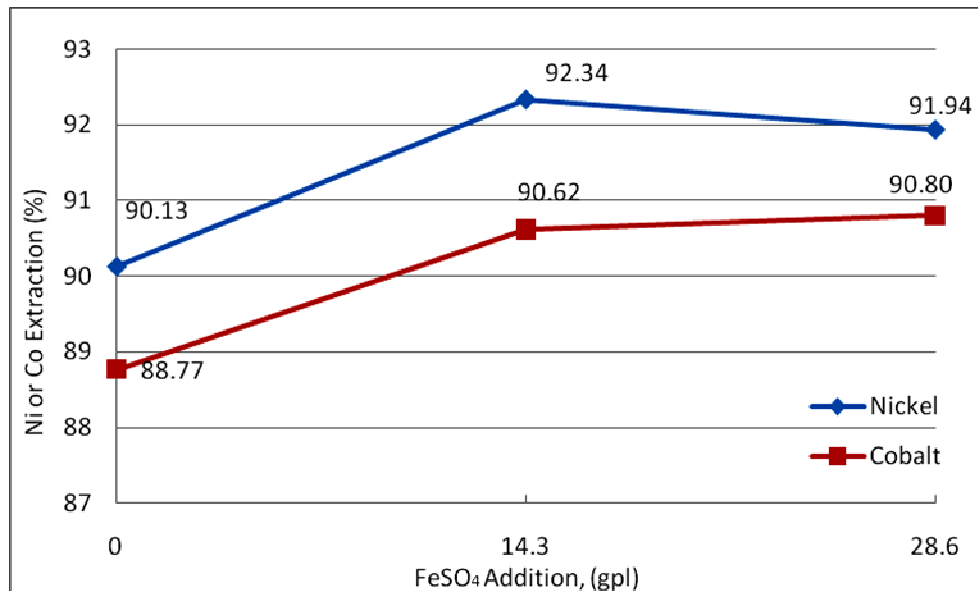


Figure 11. Effect of FeSO₄ addition on nickel and cobalt extractions

(Particle size: 100% -850 μ at 255°C leaching temperature with 300 kg sulphuric acid addition per ton of dry ore at 30% solids for one hour of leaching duration)

5. RESULTS AND DISCUSSION

When the overall experimental results were considered, it can be concluded that the nickel and cobalt extractions were affected positively with increasing temperature and duration of the high pressure leaching process. However, since these parameters constitute to be the primary operating variables of the process, the actual selection of these process parameters should be evaluated further whether the extra extracted nickel and cobalt compensate for the extra operating costs or not. One alternative might be 60 to 90 minutes of leaching at 255-260°C for at least 90% nickel and cobalt extractions. With these process parameters, ORP, or (SHE) of the pregnant leach solution would be between 400-500 mV, or (598-698 mV). From the amount of sulphuric acid determination experiments, it could be concluded that 300 kg of sulphuric acid per ton of dry ore would be enough for satisfactory nickel and cobalt extraction values together with the predetermined parameters. When the HCl addition is considered for increasing nickel and cobalt extractions, it might be a useful additive if the negative corrosive effect of HCl addition could simply be prevented. Regarding the ore feed size, it was seen that nickel extraction did not increase substantially with the extreme grinding operation. Therefore, a feed size between 100% -425 μ and 100% -1.4 mm would be a suitable feed size, and the best choice should be determined after testing the behavior of the ore for the feed size and ore settling properties after leaching. With regard to Na₂SO₄ and FeSO₄ additions, Na₂SO₄ did not seem to be effective for obtaining desirable results. However, FeSO₄ may be a good additive if its negative effects upon ore settling and filtration properties could be eliminated. Finally, the heat treatment of the ore before leaching transforms the initially easily leachable goethite mineral into difficult to leach hematite structure which results in an undesired outcome.

6. CONCLUSIONS

According to the results obtained after the high pressure acid leaching experiments, it was found that almost 90% of nickel and cobalt in the limonitic part of Gördes lateritic ore could be extracted into the leach liquor by adjusting the process parameters as follows: leaching duration between 60 to 90 minutes at 255-260°C with an acid addition of 300 kg per ton of dry limonitic ore between 100% -425 μ to 100% -1.4 mm particle size without any additives at 30% solids.

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REFERENCES

1. J.P. Golightly, 'Nickeliferous laterite deposits', Economic Geology, 75th Anniversary Volume, 710-735, 1981
2. M. Elias, M.J. Donaldson and N. Giorgetta, 'Geology, mineralogy, and chemistry of lateritic nickel-cobalt deposits near Kalgoorlie, Western Australia', Economic Geology, 76, 1775-1783, 1981
3. B.I. Whittington and D. Muir, 'Pressure Acid Leaching of Nickel Laterites: A Review', Mineral Processing and Extractive Metallurgy Review, 21:6, 527-599, 2000
4. M. Yeşil, 'Gördes Nickel Cobalt HPAL Project', The 2nd. European Nickel Conference, England, March 2010
5. S.A. Gleeson and R.J. Herrington, 'The Mineralogy and Geochemistry of the Cerro Matoso S.A. Ni Laterite Deposit, Montelíbano, Colombia', Economic Geology, 99, no. 6, 1197-1213, 2004
6. E. Büyükkıncı, Y.A. Topkaya, 'Extraction of Nickel from Lateritic Ores', M.S. Thesis, METU, January 2008

7. B.I. Whittington, J.A. Johnson, L.P. Quan, R.G. McDonald and D.M. Muir, 'Pressure acid leaching of arid-region nickel laterite ore: Part II. Effect of ore type', *Hydrometallurgy*, 70, 1-3, 47-62, 2003
8. G. Tunell and E. Posnjak, 'The Stability Relations of Goethite and Hematite, *Economic Geology*, volume 26, p. 894-898, 1931.