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LEACHING BEHAVIOUR OF A TURKISH LATERITIC ORE IN THE PRESENCE OF ADDITIVES

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Abstract: This paper investigates the dissolution mechanism of a lateritic nickel ore from the Caldag Region of Manisa in Turkey. The ore sample contained 1.2% Ni, 24.8% Fe, and 0.062% Co. The optimum leaching conditions were found to be temperature 80 ^{o}C, particle size -74 µm, H_2SO_4 concentration 200 g/dm^3, solids ratio (by weight) 10% and leaching duration 8 h. The extractions of 98.2% Ni, 98.6% Fe and Co 98.9% were obtained under these conditions. Additionally, the effects of additional substances such as NaCl, $Na_2S_2O_5$, Na_2SO_4, and KCl were investigated in order to decrease the leaching duration. The results showed that the additives accelerated the leaching kinetics and achieved nearly the same nickel and cobalt extractions at the end of 4 h compared to the results obtained after 8 h without the additives. If the additives containing chlorine were used, it was determined that the iron extraction showed no increase, although both the nickel and cobalt extractions increased.

Keywords: *laterite, nickel, agitation leaching, dissolution*

Introduction

There is a growing interest in improving the processing technology of lateritic nickel from huge reserves representing nearly 70% of the world nickel resources due to the declining nickel sulphide reserves (McDonald and Whittington, 2008). Although it is possible to process nickel sulphide ores using several methods such as flotation, the extraction of nickel from lateritic ores requires either pyrometallurgical or hydrometallurgical methods where high energy and reagent costs exist. While the cobalt content in the lateritic ores provides an economic advantage, the processing costs strongly depend on the mineralogy of the ore in which nickel can be hosted in a variety of different minerals.

Goethite is a major nickel-bearing mineral in many laterites, and nickel occurs in three modes: associated with amorphous or poorly crystalline goethite, weakly adsorbed by the crystalline goethite surface, and as a substituent in the goethite structure (Chang et al., 2010; Schwertmann et al., 1982). According to Dalvi et al. (2004), there are four different regions of the laterite profile: limonite, nontronite,

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serpentine, and garnierite. Since the nickel content of all these regions varies, the extraction methods also change.

Today, basically two processing methods are used in the industry: pyrometallurgical and hydrometallurgical methods. Pyrometallurgical processes include energy intensive techniques such as drying, calcination, and smelting. On the other hand, atmospheric leaching (AL), high pressure acid leaching (HPAL), and the Caron process are classified as hydrometallurgical processes. While the Caron process requires drying, calcination, and ammoniacal leaching, high pressure and temperature within autoclaves are necessary for HPAL. In comparison, AL is undertaken using the agitation or heap leaching methods. When hydrometallurgical methods are compared to each other, AL has considerable advantages over HPAL such as lower CAPEX and energy consumption, simpler process control, and lower maintenance costs. However, higher acid consumptions, more voluminous residue in tank leaching, slower extraction kinetics, ensuring heap permeability in heap leaching and lower nickel/iron ratios are disadvantages of AL (McDonald and Whittington, 2008; Neudrorf, 2007; Chander, 1982).

Various methods have been tried to improve nickel extraction kinetics for AL and selectivity over iron to reduce acid consumption. These comprise increasing temperature or leaching time, controlling redox potential, adding various chemicals and pre-treatment. However, all the tests performed gave similar results: high acid consumption, high dissolved iron content in pregnant leach solution, and high residual acid concentration (McDonald and Whittington, 2008; Buyukakinci and Topkaya, 2009).

Researchers have found that the addition of sodium salts showed a positive effect on the dissolution mechanism of nickel (Krause et al., 1997; Johnson et al., 2002; Whittington et al., 2003; Johnson et al., 2005). Adsorption of Ni^{2+} cations onto negative surface charged silica can be inhibited by increasing free acid amount in solution. When Na^+ ions are added to the leaching solution, competition between Ni^{2+} and Na^+ was proposed to hinder Ni^{2+} adsorption (Whittington et al., 2003). Furthermore, Johnson and Whittington (2004) used sulphate salts of Na^+, NH_4^+, and K^+ to accelerate the leaching kinetics. Although Kaya and Topkaya (2011) investigated the additions of $FeSO_4$, Cu^+, and S, the results were unsatisfactory in terms of the increasing nickel and cobalt extractions to the target levels. The addition of an oxidant, MnO_2, was tested by Loveday (2008), and provided higher nickel extraction and reduction of acid consumption.

All the additives described above were tested in the pressure leaching studies, and there were no studies carried out under AL conditions. In this study, the dissolution mechanism of a lateritic nickel ore from Caldag-Manisa (Turkey) using an atmospheric leaching method with various additives was investigated.

Materials and methods

Material characterization

A lateritic ore sample obtained from Caldag-Manisa (Turkey) was used in the tests. The chemical analyses of lateritic ore sample were performed out using Inductively Coupled Plasma (ICP) and X-Ray Fluorescence (XRF) methods, and the results are presented in Table 1. To characterize the mineralogy of the sample, polished sections were prepared, and the analyses were performed by using a JEOL – JSM 6010LV model Scanning Electron Microscope (SEM) coupled with SEM, Energy-dispersive X-ray spectroscopy (EDS). According to the results, the main source of nickel mineral was found to be goethite [(Fe,Ni)O(OH)] occurring in particle sizes up to 500 µm, which contained Fe-Mn-Ni-Co. In addition, chromite and hematite were determined as gangue minerals. The X-ray elemental maps of the sample are shown in Figs. 1 and 2. Likewise, the X-ray diffraction (XRD) analysis showed that the lateritic ore sample consisted of mainly quartz and goethite minerals while serpentine minerals were also indicated. The XRD result of the sample is given in Fig. 3.

Table 1. Chemical analyses of a representative ore sample

Component	Content (%)	Component	Content (%)
Al_2O_3	4.00	MnO	0.383
CaO	0.660	Na_2O	0.080
Co	0.062	Ni	1.20
Cr_2O_3	1.13	P_2O_5	0.028
Cu	0.001	SiO_2	40.9
Fe	24.8	TiO_2	0.130
K_2O	0.250	Zn	0.026
MgO	5.88	LOI	9.26

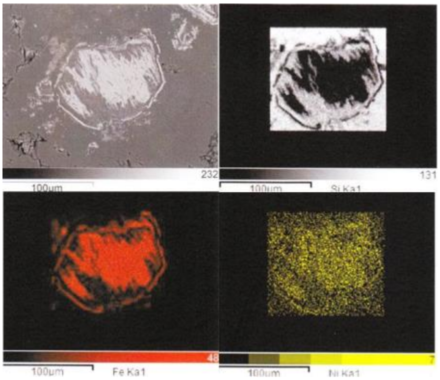

Fig. 1. X-ray elemental map of the nickeliferous limonite sample

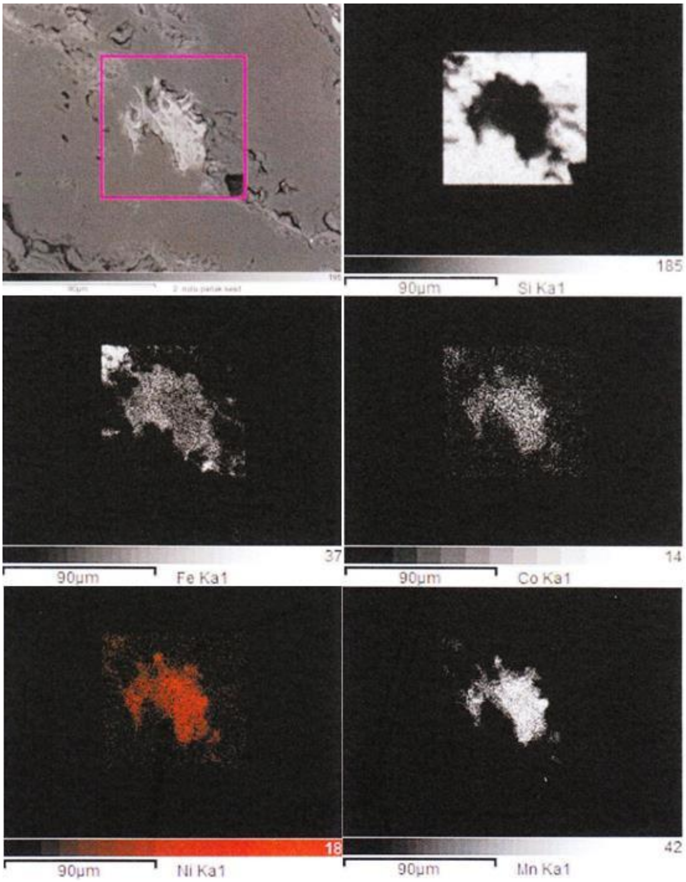

Fig. 2. X-ray elemental map of nickeliferous sample showing Fe-Mn-Ni-Co enriched zone

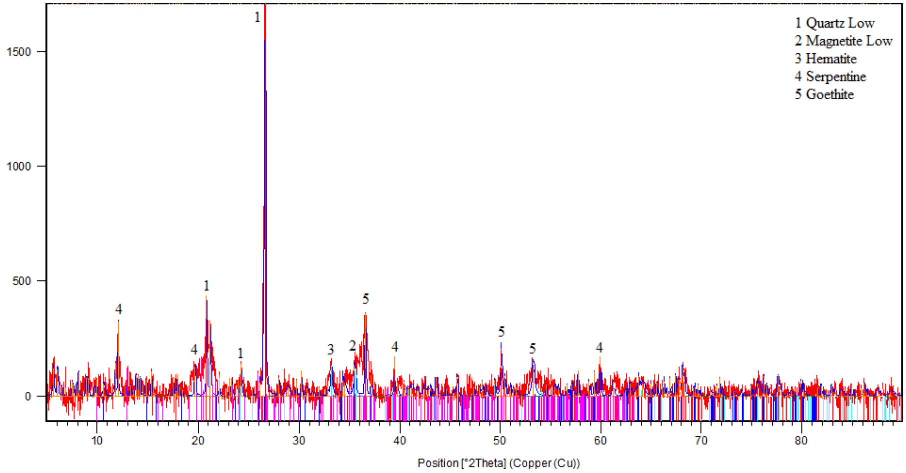

Fig. 3. XRD pattern of the nickeliferous laterite sample

Experimental

The representative sample for the agitation leaching tests was prepared using a ring mill. The leaching tests were conducted in a heated reaction vessel with Teflon® coated impeller at the speed of 500 rpm. The leaching temperature was controlled by an IKA temperature controller. The analytic grade of H_2SO_4 was used in the leaching tests. An acid resistant material was used to cover the top of the baker to prevent volatilization and help maintain the temperature during the leaching. At the end of the leaching, the leached residue was filtered and washed with water using a Buchner funnel. The dried leach cakes were analyzed. In order to determine the acid consumption, the titration was carried out with 0.1 N NaOH solution and methyl orange as an indicator.

In the agitation leaching tests, the parameters such as temperature, particle size, solid ratio (solid weight/total weight), various acid concentrations, leaching duration, and added substances were tested in detail. The added substances were included NaCl, $Na_2S_2O_5$, Na_2SO_4, and KCl. The metal extraction values were evaluated at the end of the leaching tests.

Results and discussion

Effect of temperature

In this part of the study, the leaching temperatures of 40, 50, 60, 70, 80, and 90 ^{o}C were tested to obtain higher metal extractions. The parameters of 150 g/dm^3 H_2SO_4 concentration, -100 μm particle size, 20% solids ratio were kept constant for a leaching duration of 2 h. As seen from Fig. 4, the nickel and cobalt extractions increased 44% and 37%, respectively between 40 ^{o}C and 90 ^{o}C of the leaching temperatures. On the other hand, Fe extraction increased to 55% between these temperatures. The reason for the 1.7% nickel extraction increase from 80 ^{o}C to 90 ^{o}C was attributed to the increase in the iron extraction since nickel and iron minerals were associated in the same minerals. Since the nickel extraction increased marginally at 80 ^{0}C, compared with iron extraction, 80 ^{o}C was seen to be an optimum.

Effect of particle size

In these leaching tests, the effect of particle size on the metal extractions was investigated with -300, -150, -106, -74, and -38 μm size fractions. The d_{50} and d_{90} sizes of the samples can be seen in Table 2. The experiments were carried out with 150 g/dm^3 acid concentration and 20% solids ratio at 80 ^{o}C for 2 h. According to the results shown in Fig. 5, the highest extractions were obtained with the -74 and -38 μm size fractions. This implies good mineral liberation in these fine fractions although the particle size showed no significant effect on the metal extractions. While the metal extractions were close to each other within the finer particle size fractions, based upon the higher milling costs, it was decided to continue to use the -74 μm size fraction for further tests.

Table 2. d_{50} and d_{90} sizes of the samples

Sample (μm)	d_{50} size (μm)	d_{90} size (μm)
–300	183	260
–150	62	130
–106	54	87
–74	47	68
–38	23	31

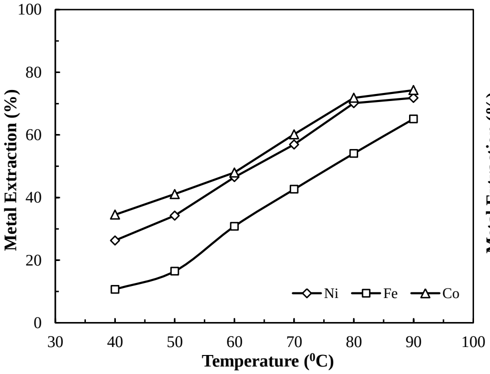

Fig. 4. Effect of temperature on metal extractions during AL of a nickeliferous laterite ore (2 h leaching duration, 150 g/dm^3 H_2SO_4, 20% solids ratio, -100 μm particle size)

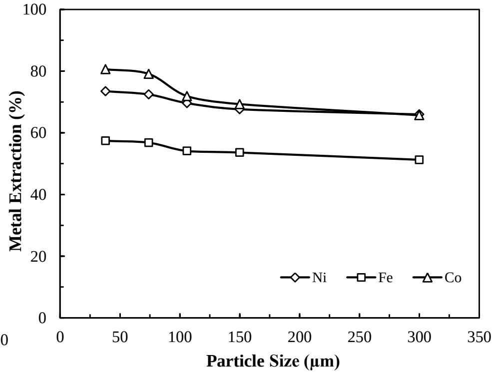

Fig. 5. Effect of particle size on metal extractions during AL of a nickeliferous laterite ore (2 h leaching duration, 150 g/dm^3 H_2SO_4, 20% solids ratio)

Effect of acid concentration on solid ratio

Up to this part of this study, all conditions were optimized at 20% solids ratio, where only Ni 72.3% and Co 79.1% extractions could be achieved. Although higher solids ratios are preferred in industrial applications to optimize plant capacity, solids ratio might be reduced in order to improve metal extractions. Therefore, the acid concentrations of 150, 200, and 250 g/dm^3 of H_2SO_4 were tested at solids ratios of 10, 20, 30, and 40%. These solids ratios were chosen to cover potential industrial application of the agitation leaching. The results shown in Fig. 6 clearly indicated that the increase in the solids ratio negatively affected nickel, cobalt, and iron extractions even with high acid concentration. In particular, the amount of the acidic solution was insufficient, especially at 40% solids ratio. As the solids ratio decreased, better results were obtained, and nearly 88% of nickel extraction could be achieved at 10% solids ratio. The results obtained with 200 and 250 g/dm^3 were similar, and therefore, 200 g/dm^3 was employed as the optimum acid concentration at 10% solids ratio.

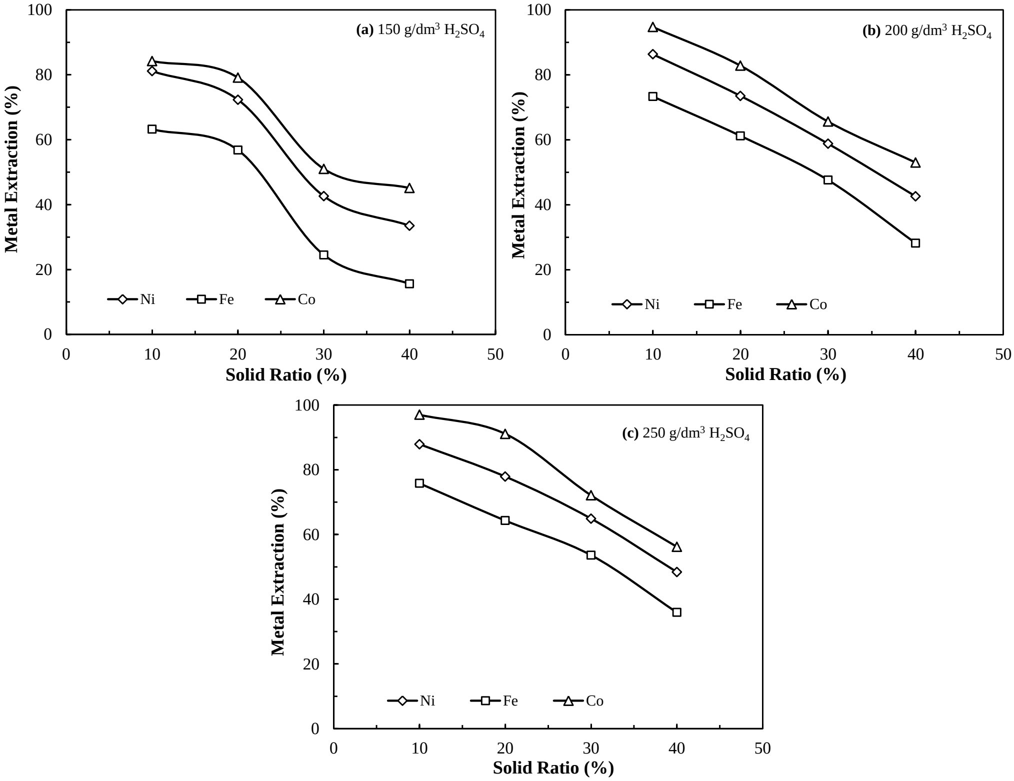

Fig. 6. Effect of solids ratio on metal extractions during AL of a nickeliferous laterite ore for an acid concentration of (a) 150 g/dm^3 (b) 200 g/dm^3 (c) 250 g/dm^3 (2 h leaching duration, –74 µm)

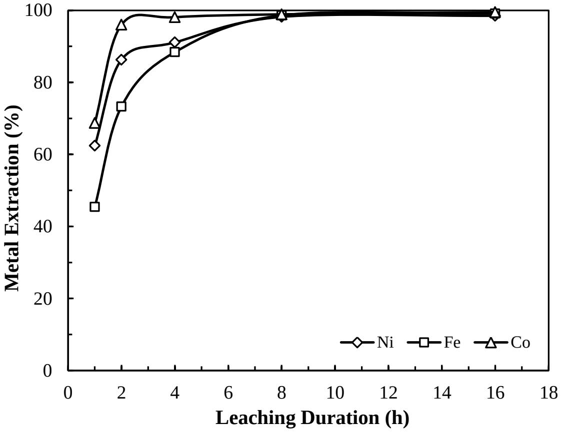

Fig. 7. Effect of leaching time on metal extractions during AL of a nickeliferous laterite ore (2 h leaching duration, 200 g/dm^3 H_2SO_4, 10 % solids ratio, –74 µm)

Effect of leaching time

The experiments were performed at various leaching times of 1, 2, 4, 8, and 16 h in order to investigate the effect of leaching time on the metal extractions. All experiments were carried out with 200 g/dm^3 of H_2SO_4 concentration, –74 µm particle size at 10% solids ratio and 80 ^oC temperature. The results of the experiments given in Fig. 7 showed that the increase of the leaching time had a positive effect on the nickel, cobalt, and iron extractions. After 8 h of the leaching time, almost all the metals were extracted. With longer leaching duration more than 8 h, a linear trend was observed.

Ultimately, Ni 98.2%, Fe 98.6%, and Co 98.9% extractions were obtained with 200 g/dm^3 of H_2SO_4 concentration at 10% solids ratio, 500 rpm agitation speed, and 80 ^oC for 8 h leaching duration. To provide these extractions under the optimum conditions determined, 928 kg/Mg of H_2SO_4 was consumed. Also, the theoretical acid consumption was calculated as 922 kg/Mg, which supported the experimental findings. In comparison with the literature, the acid consumption appeared to be very high, where Buyukakinci and Topkaya (2009) indicated that the acid consumptions were 669 kg of H_2SO_4/Mg and 714 kg H_2SO_4/Mg for dry ore nontronite and limonite, respectively. It can be concluded that the iron content in the laterite samples affects the acid consumption while limonitic ores have higher acid requirement under the atmospheric conditions. Furthermore, the pregnant leach solution contained Ni 1.31 g/dm^3, Fe 27.14 g/dm^3, and Co 0.07 g/dm^3. The extraction values obtained as a function of time indicated that nickel and iron were leached congruently.

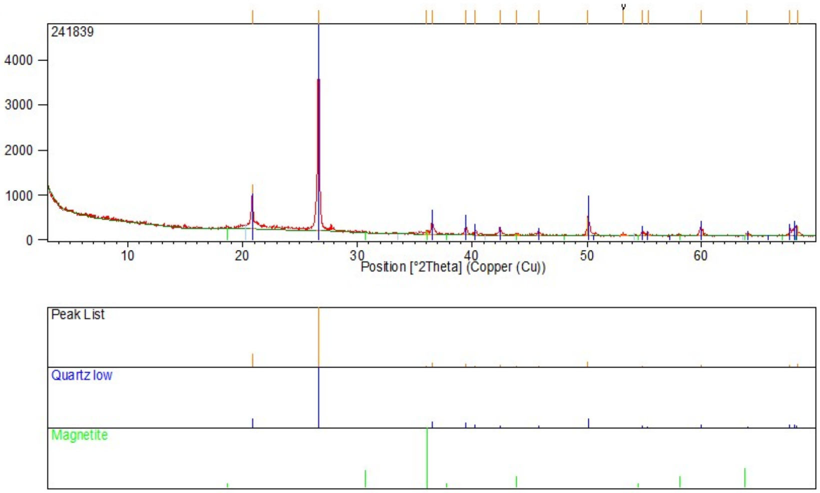

Fig. 8. XRD pattern of nickeliferous laterite leach residue

The XRD analysis was performed for the dried leach cakes, as seen in Fig. 8. In comparison to the raw ore sample, the peaks for goethite disappeared during the leaching. Furthermore, quartz and weaker magnetite peaks existed as expected since these minerals are leached poorly in the acidic medium. Additionally, the leaching of silicate minerals resulted in amorphous silica formation which was noted in the leach cake.

Effect of additives

In a series of tests, an alternative ways to increase the extraction values and/or decrease the leaching duration were investigated. The examination of the literature indicated that the addition of sodium salts in HPAL had a positive effect on the dissolution of nickel. Whittington et al. (2003) indicated that cations such as Ni^{2+} adsorbs on silica surface which has a strongly negative surface charge. This adsorption can be inhibited by an increase in the free acidity. When silica-hydroxyl sites are associated with nickel, the competition between Ni^{2+} and cations such as Na^+ can also prevent the adsorption of Ni^{2+}. On the other hand, although the association mechanism for nickel with amorphous silica is currently unknown, Whittington and Johnson (2005) reported that the reduction in nickel presenting in the hematite and silica was mostly responsible for the increase in nickel extraction. They proposed a mechanism that involves the competition between cations for adsorption on silica-hydroxyl sites.

The possibility of accelerating the dissolution during AL was investigated with various additions. Here 5, 10, 20, and 40 g/dm^3 of NaCl, $Na_2S_2O_5$, Na_2SO_4, and KCl were tested under the optimum leaching conditions except for a shorter leaching duration of 2 h. The results obtained were compared with the reference metal extractions of Ni 86.3%, Fe 73.3%, and Co 97.7% (the results of 2 h leaching without additives).

It can be concluded from the results with the use of the various additives that sodium (and potassium) salts had a positive effect on the metal extractions. With the additions, 91.4% of Ni extraction was achieved, which corresponds to a 5.1% of Ni extraction increase. The highest extractions were obtained with 10 g/dm^3 of NaCl, 20 g/dm^3 of Na_2SO_4, 5 g/dm^3 of $Na_2S_2O_5$, and 20 g/dm^3 of KCl additions (Table 3). These optimum dosages of the additives were then tested for various leaching durations. As seen from Table 4, higher nickel extractions could be obtained after 4 h in the presence of additives in comparison with the extraction values obtained without the additives. However, the iron concentrations in the pregnant solutions increased with Na_2SO_4 and $Na_2S_2O_5$ additions. In the presence of $Na_2S_2O_5$ (sodium metabisulphite), known as a reducing agent, iron was leached as Fe^{2+} rather than Fe^{3+}. Therefore, the higher overall iron extraction might be attributed to high ferrous iron content in solution. Chong et al. (2013) indicated the reduction reaction as follows:

$$MOOH_{(s)} + 3H^+_{(aq)} + e^- = M^{2+} + 2H_2O_{(l)} \tag{1}$$

$$S_2O_5^{2-} + 3H_2O_{(l)} = 2SO_4^{2-} + 6H^+_{(aq)} + 4e^- . \tag{2}$$

Mwema et al. (2002) reported the practices of using ferrous ion, copper powder, and $Na_2S_2O_5$ as the reducing agents for the leaching of trivalent cobalt oxide at Shituru plant (Congo). Also, the addition of sulphur dioxide (SO_2) as a reducing agent facilitates the acid dissolution of laterite ore resulting in high nickel and cobalt extractions (Das et al., 1997; Das and de Lange, 2011).

Table 3. Effect of various additives on metal extractions on metal extractions during AL (2 h leaching duration, 200 g/dm^3 H_2SO_4, 10% solids ratio, -74 µm particle size)

Additive	Amount (g/dm^3)	Metal Extractions (%)		
		Ni	Fe	Co
NaCl	5	89.1	76.6	98.2
	10	91.4	80.1	99.8
	20	88.4	76.1	99.5
	40	88.1	74.2	99.4
Na_2SO_4	5	83.5	72.2	97.1
	10	86.0	82.4	97.6
	20	91.4	91.9	99.8
	40	86.9	88.2	97.2
$Na_2O_5S_2$	5	89.4	87.0	98.9
	10	86.4	81.3	99.9
	20	84.5	80.5	99.5
	40	82.3	78.6	98.4
KCl	5	85.4	78.4	99.4
	10	87.5	81.7	99.5
	20	91.2	83.3	99.7
	40	87.1	81.0	99.4
Without additive	2 h	86.3	73.3	97.7

Table 4. Effect of additives on metal extractions during AL for various leaching durations (200 g/g/dm^3 H_2SO_4, 10% solids ratio, -74 µm particle size)

Additive	Duration (h)	Metal Extractions (%)		
		Ni	Fe	Co
NaCl	2	91.4	80.1	99.8
	4	96.3	80.8	99.9
	8	97.5	81.1	99.9
Na_2SO_4	2	91.4	91.9	99.8
	4	95.7	93.1	99.9
	8	97.3	94.5	99.9
$Na_2O_5S_2$	2	89.4	87.0	98.9
	4	92.6	92.1	99.9
	8	97.5	93.6	99.9
KCl	2	91.2	83.3	99.7
	4	96.4	82.7	99.8
	8	98.2	82.2	99.9
	4	91.1	88.4	98.1
Without additive	8	98.2	98.6	98.9

Conspicuously, NaCl and KCl provided higher nickel extractions with lower iron extractions when compared to the leaching tests performed without the additives. Here the presence of the chloride also appeared to suppress the extraction of iron though the reason for this is unclear.

As a result of these tests, it was shown that it is possible to perform the leaching tests for 4 h with NaCl or KCl additions instead of leaching at 8 h without the additives in order to achieve the similar nickel extractions.

Conclusion

In this study, agitated atmospheric leaching tests were conducted on a lateritic nickel ore sample, which contained Ni 1.2%, Fe 24.8%, and Co 0.062%. This process resulted in 98.2% of Ni, 98.6% of Fe, and 98.9% of Co extractions at 10% solid ratio, 500 rpm agitation speed, and 80 ^{o}C for 8 h leaching duration with 928 kg/Mg of H_2SO_4 consumption. As expected, the association of nickel and cobalt with iron in goethite was confirmed. Additional substances – NaCl, $Na_2S_2O_5$, Na_2SO_4, and KCl – were tested in order to decrease the leaching duration. Overall, the results from this study indicated that it was possible to obtain the same nickel and cobalt extractions with 16% lower iron extraction after 4 h leaching with NaCl or KCl addition in comparison with 8 h leaching without additives.

References

BUYUKAKINCI E., TOPKAYA Y.A., 2009, *Extraction of nickel from lateritic ores at atmospheric pressure with agitation leaching*, Hydrometallurgy, 97, 33-38.

CHANDER S., 1982, *Atmospheric pressure leaching of nickeliferous laterites in acidic media*, Transactions of the Indian Institute of Metals, 35, 366-371.

CHANG Y.F., ZHAI X.J., LI B.C., FU Y., 2010, *Removal of iron from acidic leach liquor of lateritic nickel ore by goethite precipitate*, Hydrometallurgy, 101, 84-87.

CHONG S., HAWKER W., VAUGHAN J., 2013, *Selective reductive leaching of oxidised cobalt containing residue*, Minerals Engineering, 54, 82-87.

DALVI A., BACON G., OSBORNE R.C., 2004, *The Past and the Future of Nickel Laterites*, PDAC International Convention, Trade Show & Investors Exchange.

DAS G.K., ANAND S., DAS R.P., MUIR D.M., SENANAYAKE G., SINGH P., HEFTER G., 1997, *Acid leaching of nickel laterites in the presence of sulphur dioxide at atmospheric pressure*, In: Cooper, W.C., Mihaylov, I. (Eds.), Proceedings of the Nickel–Cobalt 97 International Symposium: Hydrometallurgy and Refining of Nickel and Cobalt, Vol. 1.Canadian Institute of Mining Metallurgy and Petroleum, pp. 471-488.

DAS G.K., DE LANGE J.A.B., 2011, *Reductive atmospheric acid leaching of West Australian smectitic nickel laterite in the presence of sulphur dioxide and copper (II)*, Hydrometallurgy, 105, 264-269.

JOHNSON J.A., MCDONALD R.G., WHITTINGTON B.I., QUAN L.P., MUIR D.M., 2002, *Process water salinity effects in the pressure acid leaching of Cawse nickel laterite ore*, In: Peek E., Van Weert G. (Eds.), Chloride Metallurgy 2002, 1.Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 339-354.

JOHNSON J.A., WHITTINGTON B.I., 2004, *Effect of ammonium, sodium and potassium sulphates and chlorides in the pressure acid leaching of Western Australian nickel laterite ores*, In: Collins M.J., Papangelakis V.G. (Eds.), Pressure Hydrometallurgy 2004. Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 199-214.

JOHNSON J.A., CASHMORE B.C., HOCKRIDGE R.J., 2005, *Optimization of nickel extraction from laterite ores by high pressure acid leaching with addition of sodium sulphate*, Minerals Engineering, 18, 1297-1303.

KAYA S., TOPKAYA Y.A., 2011, *High pressure acid leaching of a refractory lateritic nickel ore*, Minerals Engineering, 24, 1188-1197.

KRAUSE E., SINGHAL A., BLAKEY B.C., PAPANGELAKIS V.G., GEORGIOU D., 1997, *Sulphuric acid leaching of nickeliferous laterites*, In: Cooper, W.C., Mihaylov, I. (Eds.), Proc. Nickel–Cobalt 97 International Symposium, 1.Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 441-458.

LOVEDAY B.K., 2008, *The use of oxygen in high pressure acid leaching of nickel laterites*, Minerals Engineering, 21, 533–538.

MCDONALD R.G., WHITTINGTON B.I., 2008, Atmospheric acid leaching of nickel laterites review Part I. Sulphuric acid technologies, Hydrometallurgy, 91, 35-55.

MWEMA M.D., MPOYO M., KAFUMBILA K., 2002, *Use of sulfur dioxide as reducing agent in cobalt leaching at Shituru hydrometallurgical plant*, Journal of the South African Institute of Mining and Metallurgy, (January/February), 1-4.

NEUDORF D., 2007, *Atmospheric Leaching Forum*, ALTA 2007 Nickel/Cobalt 12. ALTA Metallurgical Services, Melbourne. pp.5.

SCHWERTMANN U., 1991, *Solubility and dissolution of iron oxides*, Plant and Soil 130, 1-25.

WHITTINGTON B.I., MCDONALD R.G., JOHNSON J.A., MUIR D.M., 2003, *Pressure acid leaching of arid region nickel laterite ore Part I. Effect of water quality*, Hydrometallurgy, 70, 31-46.

WHITTINGTON B.I., JOHNSON J.A., 2005, *Pressure acid leaching of arid-region nickel laterite ore. Part III: Effect of process water on nickel losses in the residue*, Hydrometallurgy, 78, 256-263.