Beneficiation of Low-Grade Laterite Nickel by Calcination-Magnetic Separation Method

Razi, Parvane; Ahmadi, Rahman*[+]

Department of Mine Engineering, Imam Khomeini International University (IKIU),
P.O. Box 34148-96818 Qazvin, I.R. IRAN

ABSTRACT: *In this research, Effect of thermal treatment on beneficiation of low-grade laterite nickel by calcination-magnetic separation method was studied. In order to determine the components and elements of the sample, to recognize the main and minor minerals and their bond, and phase transformation caused by thermal treatment, Chemical analysis (XRF and ICP), microscopic studies and XRD analysis were done, respectively. SEM analysis was done to study the content of nickel and other minerals. In order to determine the phase transformation of the sample because of calcination treatment, thermal analysis of DTA/TG and XRD analysis, before and after of calcination were done. Wet magnetic separation tests with two methods of calcination-magnetic separation and only magnetic separation were done on the sample and the results in grade and recovery of nickel concentrate were compared. According to results, nickel content in the sample was0.94%. Main minerals of laterite sample were Hematite, Goethite, Quartz, and dolomite and minor minerals were Magnetite and minerals of serpentine group. Furthermore, there is no independent nickel mineral in the sample. SEM studies declared that nickel was substituted in iron-containing minerals (Hematite and Goethite). XRD and thermal analysis (DTA/TG) showed that at 350 °C, Goethite transformed to Hematite and at 750 °C, Hematite transformed widely to Magnetite. Calcination of feed at 750°C followed by wet magnetic separation with the magnetic field of 6000 Gauss in comparison with alone magnetic separation caused an increase in recovery and grade of magnetic concentrate to 12.7% and 0.41%, respectively. Results showed that an increase in temperature of more than 750 °C, caused a decrease in recovery and grade of nickel in magnetic concentrate.*

KEYWORDS: *Phase transformation; Calcination; Nickel laterite; Magnetic separation*.

INTRODUCTION

More than 70% of the world's nickel ores are laterites and about 30% of them are sulfides, but the majority of nickel production is from laterite reserves [1]. One big problem in the way of extracting nickel from laterites is an unequal distribution of nickel in the ore body [2]. On the other hand, the existence of other metals such as silica will cause some difficulties in the beneficiation process of laterites [3]. In the past decade, nickel production from sulfide, reserves reduced and recently reached a constant amount. With the increasing need for nickel all over the globe, laterite nickel will become the main source for nickel production [4].

* *To whom correspondence should be addressed.*
+ E-mail: r.ahmadi32@gmail.com
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There are different methods for beneficiation of laterite nickel. Extraction of nickel from low-grade reserves usually is done by with metallurgical methods such as pyrometallurgy, hydrometallurgy, and physical methods. In approximately all of the pyrometallurgical processes three thermal phases exist, which are drying, reduction and smelting [5]. Smelting is one of the pyrometallurgical processes, which is used for primary beneficiation of silicate laterites that contain 2% nickel [6].

There are various hydrometallurgical processes for nickel production, but only high-pressure acid leaching and Caron process are capable of massive production in the industry [6,7].

Caron method produces the best results with limonite ores or limonite and saprolite mixtures. Furthermore, the efficient nickel grade with this process is between 1 and 1.7% [8].

High-pressure acid leaching is more common because in comparison with Caron process consumes lower energy, so has a lower price for each tone of produced nickel [9,10].

With consideration of previous studies more than one process is necessary for improving the nickel grade and recovery [11]. Processes like calcination or roasting in presence of coal or sodium sulfate and then beneficiation of the sample had been used before. These kinds of methods will change the mineralogical structure of laterite, and then improve the recovery and grade of produced nickel [12, 13]. Roasting in comparison with calcination has two disadvantages, first roasting is a thermal process in presence of coke, coal or sodium sulfate, also after a while the transformed phase will turn to its first phase [14], but calcination is a heating treatment without the presence of any other materials and in the case of laterites, the transformed phase won't back to its first state [15].

In this research, we tried to study the effects of calcination of nickel laterite sample at high temperature before magnetic separation, which is a physical, non-destroyable and environment-friendly method. In this paper, changes, and transformations of laterite nickel because of the calcination process, results of beneficiation method with alone magnetic separation in comparison with a calcination-magnetic method in nickel recovery and grade were investigated.

EXPERIMENTAL SECTION

A low-grade sample of laterite nickel was taken from Chahgheib deposit located in Bavanat-Fars province, Iran. First, ore was crushed to -150 µm with two crushing steps (jaw and cone crushing) and after that, a milling step with a laboratory wet rod mill (steel rods with 27.7 mm diameter and 243 mm length)was done (One-kilogram sample with one-liter water for 10 minutes). The chemical composition of the sample was analyzed with X-Ray Fluoresce (XRF) model PW1800 and Inductively Coupled Plasma (ICP) model Liberty-RL, Varian company. Also, phase transformations in the due to sample because of thermal treatment was determined with X-Ray Diffraction (XRD) model PW1800 Philips Company, Netherland.

In XRD analysis, copper lamp, the 2θ angle between 10° and 80°, the scan speed of 2°/min were used. Microscopic mineral studies were done in two fractions of -150+75 µm and -75 µm with Polarizan light microscope Zeiss model Axioplan, Switzerland. Also, Scanning Electronic Microscope (SEM) model LEO 1430 VP, Germany and England was used for studying the phases containing nickel and phase transformations before and after of thermal treatment. For studying the sample with a scanning electronic microscope, 25 mm diameter thin circular polished sections were used. For preventing from charging the sample (because of isolation, electrons would accumulate on the surface and preventing from taking images and analysis), the surface of the sample was covered with a thin carbon layer (about 10 nm) with a carbon covering device.

After preparation of the sample, the sample was kept in a special holder and put into the device. Furthermore, thermal analysis (DTA/TG) was done with thermal analysis device model STA 409 PC Luxx made in Germany. For this purpose, 100 gram of sample with a size of -150µm was prepared. Thermal analysis was done in the presence of alumina as reference material at a heating rate of 0.16°/sand at a temperature range of 0-1000 °C.

Beneficiation of laterite nickel was done with wet magnetic separation device made of Boxmag Rapid limited co, England. For doing these tests, laboratory rod mill product was used in each test. Magnetic separation tests were done in different magnetic fields from 1000 to 8000 Gauss. In some of the tests, before magnetic separation, the first sample was calcined in a muffle furnace model AWF 12/25 made in Lenton England in temperatures between 350 and 900°C during 60 min followed by magnetic separation. At the end of each test, magnetic and non-magnetic sections were analyzed for nickel content with ICP-IES device.

Table 1: Chemical composition of laterite nickel sample (XRF (Wt%)).

Constituent	NiO	MnO	Fe_2O_3	Cr_2O_3	CaO	SiO_2	Al_2O_3	MgO	L.O.I
Content	1.19	0.29	42.87	3.11	4.40	28.69	4.50	3.71	11.27

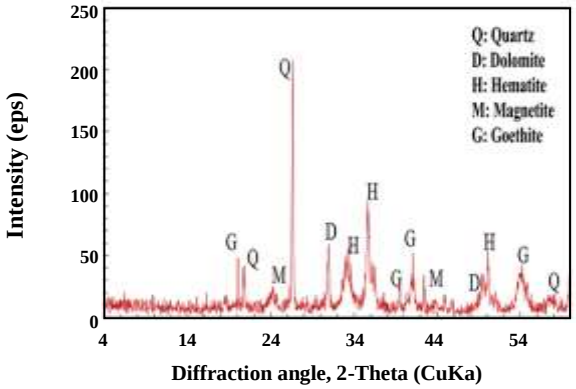

Fig. 1: XRD analysis of laterite sample.

RESULTS AND DISCUSSION

XRF and ICP analysis

XRF chemical analyses results are given in Table 1. According to analysis results, the sample contains 1.19% NiO, 42.87% Fe_2O_3, 3.71% MgO and 28.69% SiO_2. According to ICP analysis, a nickel content of the sample is 0.94%, which this amount states that the sample is low-grade.

XRD Analysis

XRD pattern of the nickel laterite sample is given in Fig. 1. XRD analysis shows that minerals with crystal structure are Quartz (SiO_2), Dolomite($CaMg(CO_3)$), Hematite (Fe_2O_3), Goethite (FeOOH) and a little amount of Magnetite (Fe_3O_4). Furthermore, according to this analyze there is no crystal ore that contains nickel. The absence of nickel peak in XRD graph can be attributed to the presence of amorphous nickel or low amount of nickel in the sample, which makes impossible to detect it.

Microscopic studies of ore

Images of microscopic studies of the sample are shown in Fig. 2. Microscopic studies showed that the sample contains metallic minerals such as Magnetic, Hematite, Goethite and non-metallic minerals such as Quartz, Dolomite and Serpentine group.

Findings of microscopic studies were similar to XRD analysis and showed no independent primary nickel mineral. According to these studies, Hematite and Goethite are the main iron minerals; which contain nearly 40-45% v/v of the sample according to microscopic studies.

Fig. 2 illustrates three microscopic images of nickel laterite sample for three size fractions. Based on the achieved information from microscopic images some of the hematite particles are binary composites and have substituting texture in magnetite. Some of the goethite particles are free and have zoning with hematite, which in most cases are spherical or fractured segments. The sample contained less than 10% magnetite. Cavities and fragments of hematite-goethite are filled with gangue minerals such as quartz and dolomite.

Scanning Electron Microscopy Analysis (SEM)

Fig. 3 shows the SEM images of the nickel sample. Fig. 3(a) shows the periodic zoning of hematite and magnetite and Fig. 3(b) shows the Map analyze of nickel at two sections of one hematite-magnetite nodule. In SEM analyze, The Back scatter electron detection system was used. In this system, darker areas, shows lighter compounds and brighter areas show the heavier compounds. So in Fig. 3(a), darker area is hematite and the brighter area is magnetite. As can be seen in Fig. 3(b), nickel exists in both hematite and magnetite, but nickel amount in hematite part is more than magnetite part, also it is obvious that the nickel laterite sample is low grade. Furthermore, for approving the results of SEM analysis and exact appointment of the nickel and the number of other elements in different particles of the sample EPMA analysis were done.

Electron Microprobe Analysis (EPMA)

Fig. 4 indicates the images of the sample during EPMA analysis. In this analysis, 25 regions of the sample were selected and the amount of nickel, manganese, silica, chrome and their oxides were measured.

It was obtained that the highest amount of nickel is 1.09% and in region number 7. After that, regions number 19, 17 and 9 with 0.62, 0.55 and 0.43 %Ni, respectively. The least nickel existed in regions number 5 and 6 with 0.01% Ni. The highest amount of iron is 69.08 Ni in region number 8 and region number 7 have the most silica

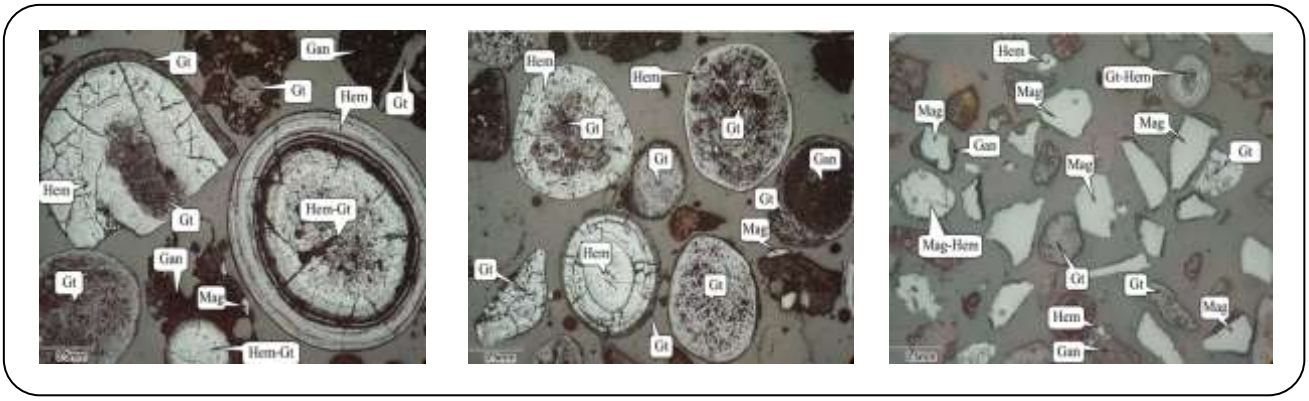

Fig. 2: Hem: hematite, Mag: magnetite, Gt: goethite and Gan: gangue particles at (a) +841µm (b) +595µm (c) +74µm.

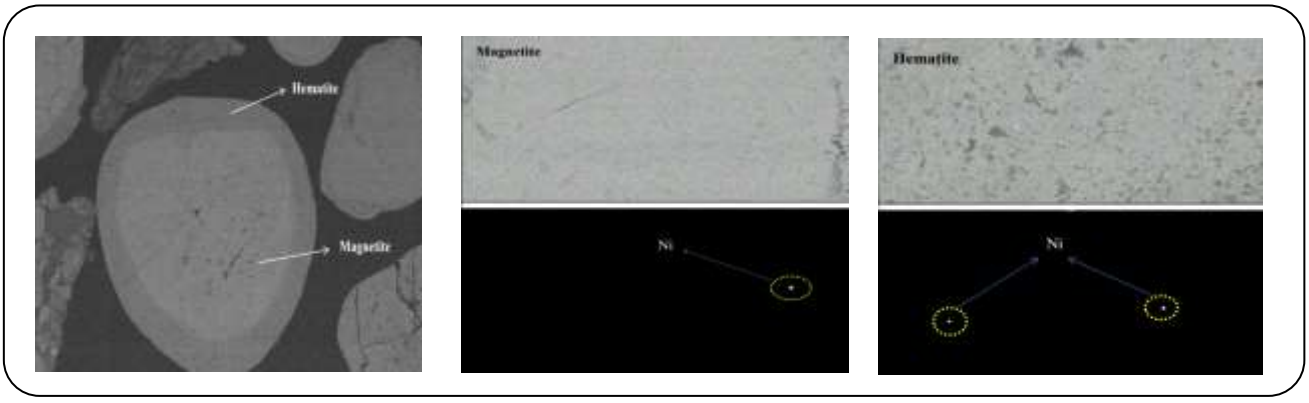

Fig. 3: SEM images of(a) hematite-magnetite nodule and (b) Map scanning of two sections of hematite and magnetite.

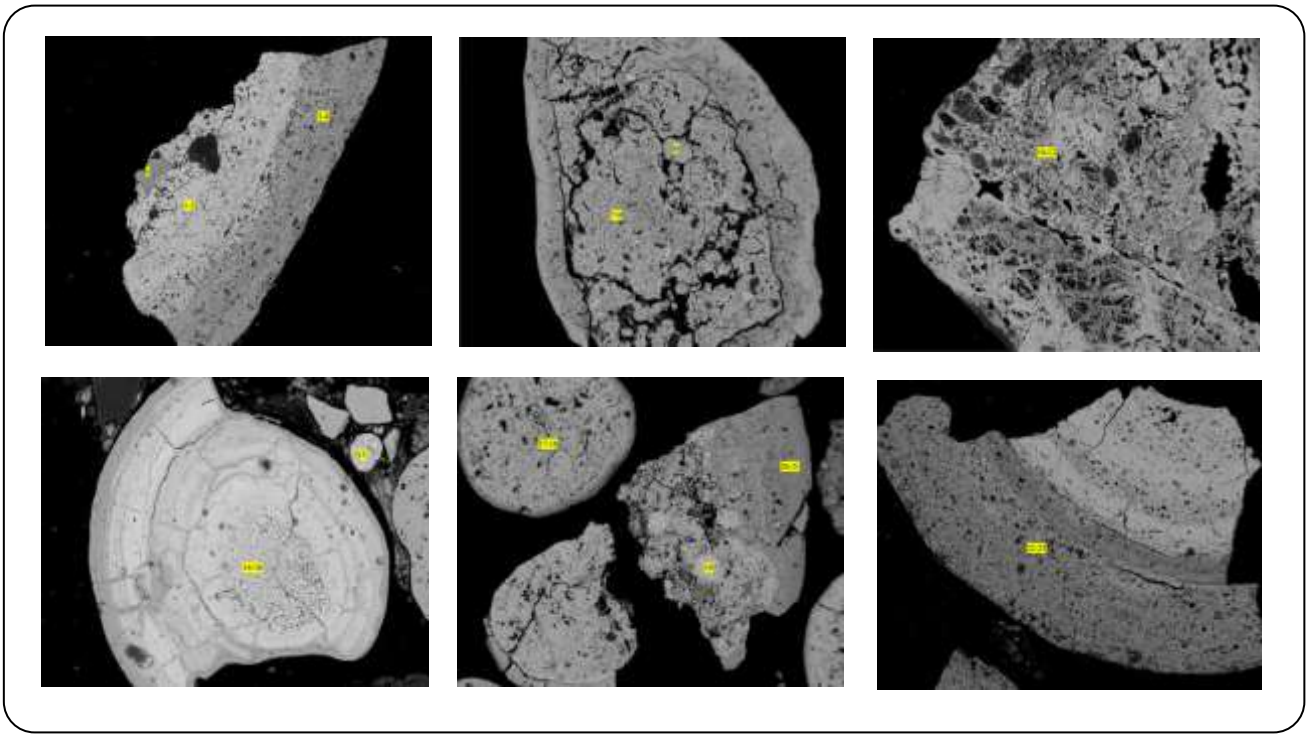

Fig. 4: EPMA images of the nickel laterite sample.

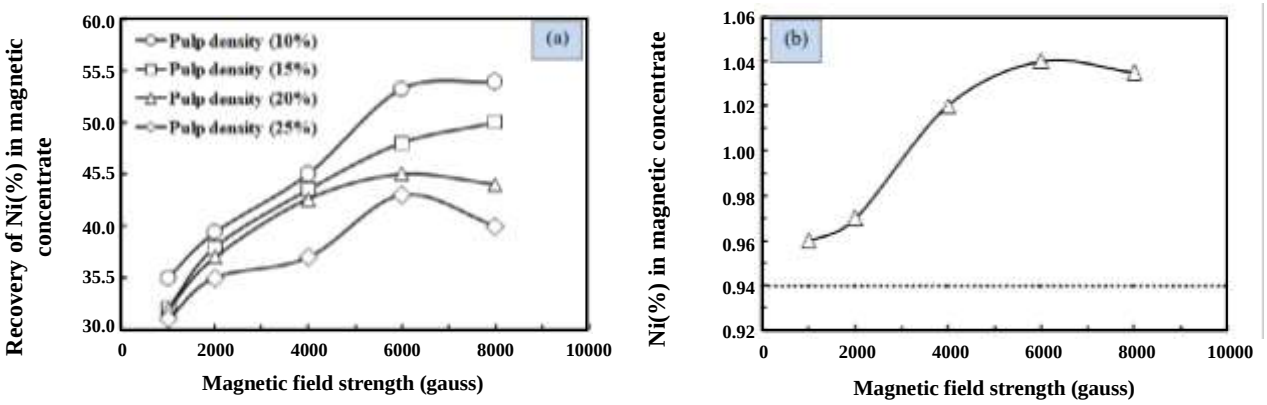

Fig. 5: (a) Effect of the magnetic field and pulp density on recovery and (b)Effect of magnetic field on nickel grade in magnetic concentrate.

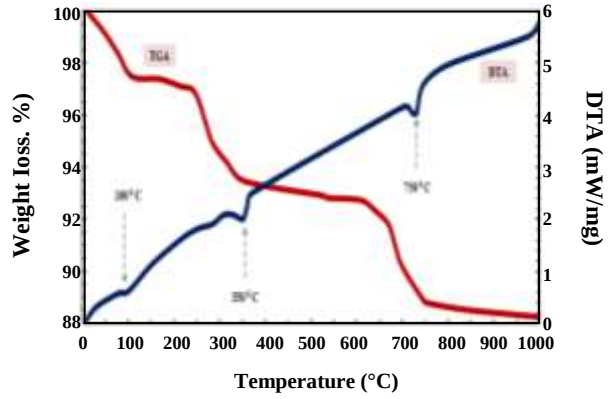

Fig. 6: DTA/TG pattern of nickel laterite sample

in it (7.79%). It has to be mentioned that these results are similar to SEM analysis, which means that the sample is low grade and the highest nickel content, in decreasing order, is in hematite, goethite and magnetite particles.

Beneficiation of nickel with a magnetic separation method

Wet (because of the particle size of the sample) magnetic separation tests were done on nickel samples with d100 = 105µm size and 10%pulp density to 25% in magnetic fields of 1000 to 8000 Gauss. Fig. 5(a), shows the nickel recovery changes vs magnetic field and pulp density. According to the figure, with increasing magnetic field from 1000 to 8000 Gauss in pulp density of 10%, nickel recovery in concentrate increases from 35% to 53.9%. With increasing the magnetic field, magnetic force on particles increases and the probability of absorption of magnetic particles will increase. Also, the figure shows that with increasing the pulp density to 25%, nickel recovery in concentrate decreases. Furthermore, decreasing the recovery with increasing pulp density in a higher magnetic field is more than lower magnetic fields. In lower pulp densities because of more proper dispersion and distribution, particles easily absorb to the magnetic poles and recovery increases. Also, according to Fig. 5(b) nickel grade in concentrate with an increase in magnetic field from 1000 to 8000 Gauss had increased from 0.96% to 1.04%. With achieved grade and recovery, the magnetic field of 6000 Gauss and pulp density of 10% was selected as optimum conditions.

Effect of calcination on magnetic separation

In order to study the effect of thermal treatment on recovery and grade of magnetic concentrate, laterite nickel sample was calcined before the magnetic separation in different temperatures. DTA/TG analysis, which is a strong instrument for analyzing thermal features of materials and their phase transformations, was used for analyzing the phase features of nickel laterite in different temperatures.

As can be seen in Fig. 6, calcination of laterite sample can cause three endothermal reactions. In DTA/TG curves concave peaks illustrate endothermal reactions. First, endothermal reaction is the removal of sample moisture at 100°C and weight reduction equal to 1%. Second endothermal reaction at 350°C, caused a weight reduction of 2% and transformation of Goethite to Hematite occurs. According to *Keskinkilic et al* studies [16], the phase transformation of Goethite to Hematite as a result of calcination at 350°C is proved.

This transformation has been subjected to a number of investigations and there has been no general agreement on the mechanism [17]. According to the studies carried

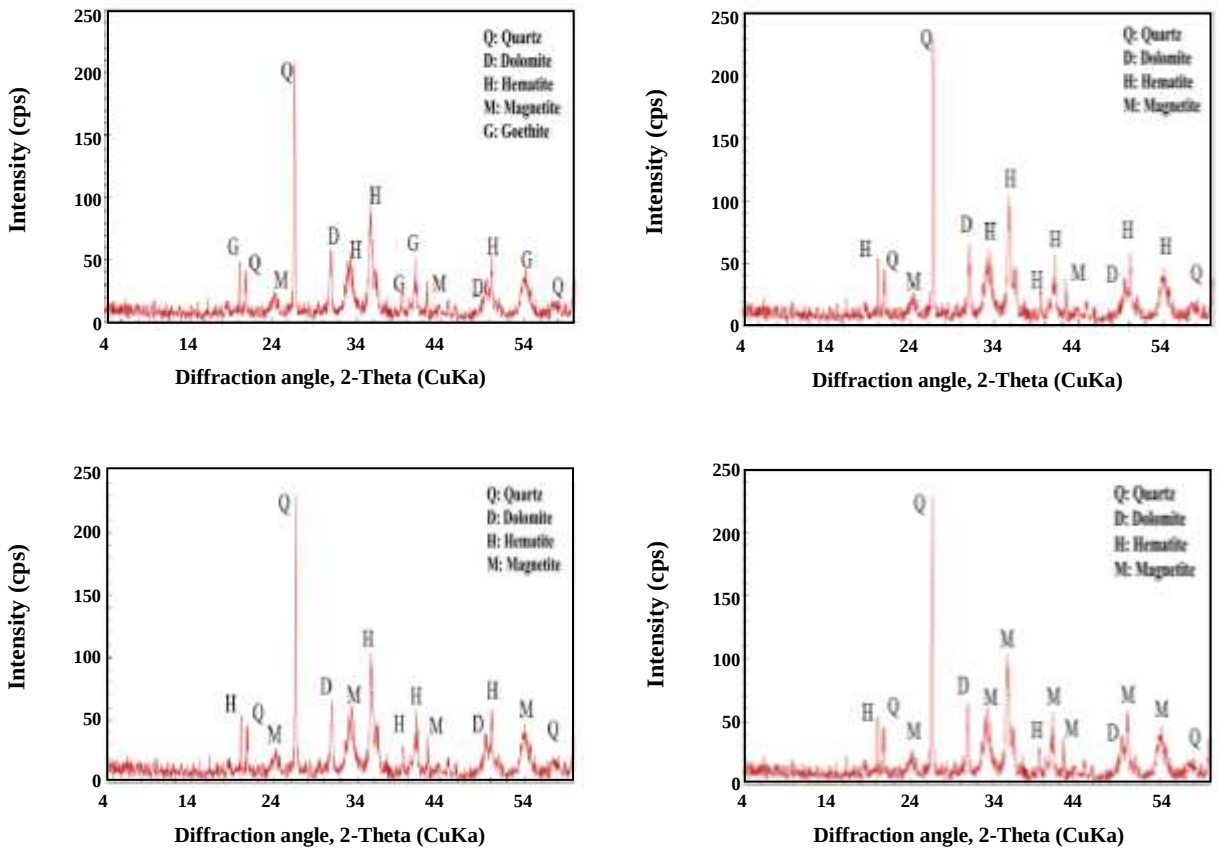

Fig. 7: XRD analysis of treated sample at different temperatures (a) without calcination, (b)350°C, (c)650°C, (d)750°C.

out by *Walter et al.* [18] and *Watari et al.* [19], the transformation is suggested to take place directly according to reaction [1]:

$$2\alpha(\mathrm{FeOOH}) \rightarrow \alpha(\mathrm{Fe_2O_3}) + \mathrm{H_2O} \quad (1)$$

On the other hand, some researchers [20-21] propose that an intermediate phase, known as proto-hematite or hydro hematite, forms before the final formation of hematite.

But the most weight reduction equal to 4% at 750°C occurred, which caused the phase transformation of Hematite to Magnetite. According to the figure, with increasing temperature to 1000°C new phase transformations did not occur to the laterite sample.

Fig. 7 shows phase transformations of nickel sample calcined at 350, 650 and 750°C with XRD patterns. According to the figure at all temperatures, Quartz and Dolomite minerals remained unchanged. With calcination of the sample at 350°C, Goethite transformed to Hematite. With increasing temperature to 650°C low phase transformation of Hematite to Magnetite occurred. More increase in temperature to 750°C caused extent phase transformation of Hematite to Magnetite.

Fig. 8 shows SEM images of nickel laterite sample that contains Hematite and Goethite before and after of calcination at 750°C during 3600 s. Bright magnified points in left figure (after calcination) with SEM images assistance detected as magnetite phase with a spherical shape and maximum size of 100µm. the calcination temperature is a key parameter in growing the magnetite particles and becoming spherical. In this way with increasing the temperature to a special limit (about 750°C), magnetite particle sizes increased and became spherical. This point is approved by *Zhu et al.* [22], too.

The authors believe that during calcination, the phase transformation of hematite to magnetic happens. In other words, the main chemical bonds in nickel-containing minerals are ionic and covalent bonds [23, 24]. As the formation of ionic bonds among atoms in the mineral structure is increased, the polarity of bond increases,

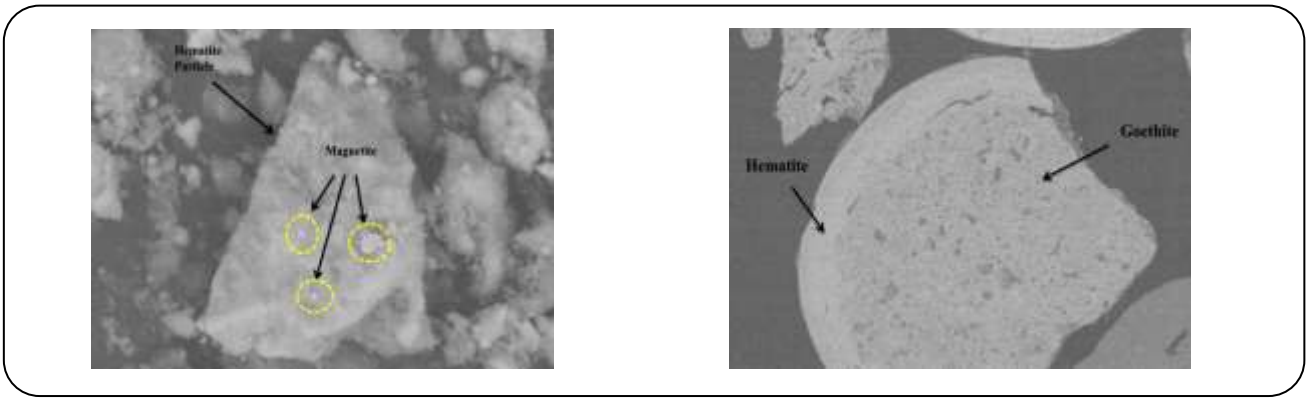

Fig. 8: SEM images of laterite sample, Before (Right) and after (Left) during 60 minutes calcination at 750°C.

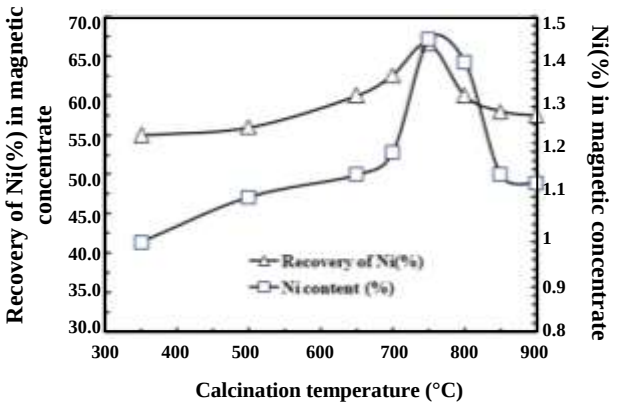

Fig. 9: Effect of magnetic field on grade and recovery of nickel concentrate at different calcination temperatures.

and the bond fractures easily. By contrast, as the formation of covalent bonds is increased, the degree of non-polarity increases, and the bond fractures difficultly. The chemical properties of nickel laterite sample show that during the calcination process, Ni-O, Fe-O, and Mg-O bonds fracture prior to Si-O bonds [22]. It means that during the reduction of nickel laterite, Ni^{2+} and Fe^{2+} are reduced to metallic iron and nickel and Ni-O and Fe-O bonds fracture, which destroys the lattice of hematite. The produced metallic iron and nickel existing in the pore of lattice have a lower melting point and higher fluidity at high temperatures. Thus, they are energetically active and assemble to form Fe-Ni metallic particles. These particles show better separation in beneficiation processes mainly wet magnetic separation process. Temperatures higher than 1023 K can cause disintegration of magnetite particles formed in hematite.

In order to investigate the effect of temperature on magnetic separation, seven samples with -105µm size each with 500-gram weight within a furnace at 350, 650, 700, 750, 800, 850 and 900°C were calcined for 3600 s. Then 100 gram of each sample was analyzed and weight reductions of samples were determined. Magnetic separation tests were done On 400 grams remained samples. Weight reductions of samples were between 5.25% and 10.85%. The optimum magnetic field strength in these tests was 6000 Gauss and other conditions were similar to previous tests.

Fig. 9 shows the effect of calcination on nickel recovery at different temperatures. According to the figure with increasing the calcination temperature from 350 to 750°C nickel recovery in concentrate will increase from 55.0% to 66.6%. With more increase in temperature to 900°C, nickel recovery decreases and reaches to 57.5%.

Furthermore, according to the figure with increasing the temperature from 350 to 750°C nickel grade in magnetic concentrate increases from 1% to 1.45%. More increasing in temperature decreases nickel grade to 1.15% and at 900°C to 1.13%.Temperatures higher than 750°C can cause disintegration of magnetite particles formed in Hematite and with fining the magnetite particles probability of getting trapped within a magnetic field can cause a decrease in grade and recovery of nickel in concentrate (fine particles role).

CONCLUSIONS

In this research, the effect of thermal treatment (calcination) on magnetic separation of low-grade laterite nickel sample was studied. According to the results, there was no independent nickel mineral in the laterite sample and nickel exists as a substitution element in other iron

containing ores such as Hematite and Magnetite. Nickel grade of the sample according to ICP analysis was 0.94%. Wet magnetic separation on calcined feed showed that with an increase in calcination temperature to a special range, nickel recovery and grade will be increased. Under optimized condition magnetic field 6000 Gauss and a calcination temperature of 750°C, nickel grade and recovery in magnetic concentrate in comparison with alone magnetic separation will be increased about 0.41% and 12.7%, respectively. According to achieved results from the thermal analysis, XRD and SEM, Increasing grade and recovery of nickel in magnetic concentrate, occurred as a result of Goethite to Hematite transformation at 750°C and followed by phase transformation of Hematite to Magnetite at 750°C. Calcination, more than the transformation of Goethite to Hematite to spherical Magnetite(with a maximum particle size of 100µm), which have special magnetic properties, caused increased in iron-containing ore surfaces and this phenomenon caused an increase in metallurgical recovery of magnetic separation.

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REFERENCES

[1] Yang J., Zhang G., Ostrovski O., Jahanshahi Sh., Changes in an Australian Laterite ore in the Process of Heat Treatment, *Minerals Engineering*, **54**: 110-115(2013).

[2] Abedini A., Calagari A.A., The mineralogy and Geochemistry of Permian Lateritic Ores in East of Shahindezh, West-Azarbaidjan Province, *Iranian Society of Crystallography and Mineralogy*, **20**(3): 59-73(2012).

[3] Dalvi A., Bacon G., "The Past and the Future of Nickel Laterites", *PDAC 2004 – International Convention, Trade Show & Investors Exchange*, 7-10 March (2004).

[4] King M., "Nickel Laterite Technology - Finally a New Dawn", *JOM*, 35-39(2005).

[5] Onodera J., Inoue T., Imaizumi T., Attempts at the Beneficiation of Lateritic Nickel Ore, *International Journal of Mineral Processing*, **19**: 25-42(1987).

[6] Li J., X., Hu Q., Wang Z., Zhou Y., Zheng J., Liu W., Li, L., Effect of Pre-Roasting on Leaching of Laterite, *Hydrometallurgy*. **99**(2):84-88(2009).

[7] Valix M., Cheung W.H., Study of Phase Transformation of Laterite Ores at High Temperature, *Minerals Engineering*, **15**:607-612(2002).

[8] Sedigh M., "Recovery of Nickel from Fars-Bavanat Laterite Reserve", Postgraduate Thesis, Engineering Faculty, University of Tehran(2013).

[9] Buyukakinci E., Topkaya Y.A., Extraction of Nickel from Lateritic Ores at Atmospheric Pressure with Agitation Leaching, *Hydrometallurgy*, **97**: 33-38 (2009).

[10] Rhamdhani M.A., Hayes P.C., Jak E., Nickel Laterite Part 2-Thermodynamic Analysis of Phase Transformations Occurring During Reduction Roasting, *Mineral Processing and Extractive Metallurgy*, **118**(2009).

[11] Agacayak T., Zedef V., Dissolution Kinetics of a Lateritic Nickel ore in Sulphuric Acid Medium, *Acta Montanistica Slovakia*, **17**:33-41(2012).

[12] Guo X., Shi W., Li D., Tian Q., Leaching Behavior of Metals from Limonitic Laterite ore by High Pressure Acid Leaching, *Transactions of Nonferrous Metals Society of China*, **21**:191-195(2011).

[13] McDonald R.G., Whittington B.I., Atmospheric Acid Leaching of Nickel Laterites Review Part I. Sulphuric Acid Technologies, *Hydrometallurgy*, **91**:35-55(2008).

[14] McDonald R.G., Whittington B.I, Atmospheric Acid Leaching of Nickel Laterites Review. Part II. Chloride and Bio-Technologies, *Hydrometallurgy*, **91**:56-69(2008).

[15] Curlook W., "Direct Atmospheric Leaching of Saprolitic Nickel Laterites with Sulfuric Acid", In: Imrie, W.P., Lane, D.M. (Eds.), *International Laterite Nickel Symposium.* TMS, Warrendale, 385–398(2004).

[16] Keskinkilic E., Pournaderit S., Geveci A., Topkaya Y., Calcination Characteristic of Llaterite Ores from the Central Region of Anatolia, *The Journal of the Southern African Institute of Mining and Metallurgy*. **112**: 877-882(2012).

[17] Prasad P.S.R., Prasad K.S., Chaitanya V.K., Babu E.V.S.S.K., Sreedhar B., Murthy S.R., In-Situ FTIR Study on the Dehydration of Natural Goethite, *Journal of Asian Earth Sciences*, **27**:503–511(2006).

[18] Walter D., Buxbaum G., Laqua W., The Mechanism of the Thermal Transformation from Goethite to Hematite, *Journal of Thermal Analytical and Calorimetry*, **63**:733–748 (2001).

[19] Watari F., Delavignette P., Amelinckx S., Electron Microscopic Study of Dehydration Transformation. II, *Journal of Solid State Chemistry*, **29**: 417–427(1979).

[20] Gualtieri A.F., Venturelli P., In-Situ Study of the Goethite-Hematite Phase Transformation by Real Time Synchrotron Powder Diffraction, *American Mineralogist*, **84**: 895-904 (1999).

[21] Ozdemir O., Dunlop J.D. Intermediate Magnetite Formation During Dehydration of Goethite, *Earth and Planetary Science Letters*,**177**: 59-67 (2000).

[22] Zhu D.Q., Cui Y., Hapugoda S., Douglas J., Upgrading Low Nickel Content Laterite Ores Using Selective Reduction Followed by Magnetic Separation', *International Journal of Mineral Processing*, : 106-109 (2012).

[23] Lebid M., Omari M., Effects of the Solvent and Calcination Temperature on $LaFeO_3$Catalysts for Methanol Oxidation, *Iranian Journal of Chemical and Chemical Engineering (IJCCE)*. **35**(3):75-81(2016).

[24] Ilschner B., Grant N.J., Russell K.C., "Materials Beneficiation", Springer-Verlag Inc., New York (1991).