NICKEL PIG IRON PRODUCTION FROM LATERITIC NICKEL ORES

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ABSTRACT

Nickel is mainly used as ferronickel in stainless steel production industry. Its usage as low grade ferronickel or nickel pig iron (NPI) in stainless steel production is a relatively new trend to reduce the cost of high grade ferronickel. In this study, low grade lateritic nickel ores were processed by using carbothermal reduction to produce NPI. The used ore was from Turkey East Anatolian region. In the first experimental set, raw lateritic ore containing 0.9% Ni, 0.054% Co and 2.3% Cr was mixed with metallurgical grade coke at different stoichiometric ratios. The samples were smelted at 1600-1650 ^{o}C temperature range in an induction furnace for 25 minutes. In the second experimental set, different process times were examined varying from 15 to 35 minutes. The effect of CaO addition to the smelting charge was also investigated in the last experimental set. Raw materials, obtained alloy and slag phases were characterized by using XRD (X-Ray Diffractometer), XRF (X-Ray Fluorescence Spectrometer) and AAS (Atomic Absorption Spectrometer) techniques.

KEYWORDS: *Lateritic nickel ores, nickel pig iron.*

INTRODUCTION

Nickel is a very important metal which is widely used in the industry. Refined metal, powder and sponge forms are the main end-product types. The most remarkable consumption area is stainless steel industry as 62% of metallic nickel. It is followed by super alloy and nonferrous alloy production as 13% in accordance with its superior corrosion and high temperature properties [1, 2, 3].

Nickel ores can be subdivided into two groups as sulphide ores and lateritic ores. Despite the fact that 70% of land based nickel ores are lateritic, 60% of primary production is from sulphide ores [1, 2, 4, 5]. The importance and use of lateritic ores are increasing due to the increase in nickel prices and decrease in the reserves of sulphide ores. Laterite nickel ores typically occur in tropical or sub-tropical regions consisting of weathering of ultramafic rocks which contain iron and magnesium in high levels. These deposits usually exhibit different layers due to weathering conditions such as a silica rich layer, a limonite layer [dominated by goethite [$FeO(OH)$] and hematite (Fe_2O_3)] and a saprolite [$(Ni,Mg)SiO_3.nH_2O$)] layer rich in magnesium and basal elements. Lastly there are altered and unaltered bed rocks. Between the saprolite and limonite layer there is usually a magnesium rich transition layer (10-20% Mg) with iron which is called serpentine [$Mg_3Si_2O_5(OH)_4$]. For an ideal laterite deposit, the limonitic layer is not very suited for upgrading, while upgrading the magnesium-rich saprolitic layer is also limited for the nickel concentration [1, 2, 3, 6, 7, 8].

Several common pyrometallurgical, hydrometallurgical and combined (pyro-hydrometallurgical) methods are performed for the extraction of nickel from lateritic ores. High temperature pressure acid leaching (HPAL) is generally used to recover metallic nickel and cobalt from laterite nickel ores. It is more suitable for the plants processing ores with low magnesium oxide and aluminum oxide content. Lateritic ores are exposed to hot acidic leaching around ~250 °C to dissolve nickel and cobalt under high pressure. The process is followed by solvent extraction(SX) [6, 9, 10], however this method is not commercially used at present. The main disadvantage for HPAL is the high cost of titanium autoclaves and maintaining costs. Process is complex and difficult to control due to the high pressure and the heating of the process [4, 6, 10]. Atmospheric leaching (AL) is being replaced with HPAL due to the low cost and more suitable for the smaller scale plants. AL includes direct leaching of laterite ores in the organic or inorganic acids and obtaining Ni, Co in the solution. Solution can be enriched by using SX and metallic nickel and cobalt are recovered by using electro wining (EW) or precipitation [4, 6, 9]. Caron Process was first developed by Caron in the 1920s however this process was firstly used after World War 2nd in Cuba. This process can be applied to high iron limonitic ores and tolerates more Mg than other acid leaching processes. The process comprises blending, drying, reduction in a roaster (Product is generally iron-nickel alloy), quenching in ammoniacal ammonium carbonate solution and Ni and Co precipitation steps. The recovery is low when it is compared with pyrometallurgical and hydrometallurgical processes. The first step of the process also consumes high energy [10, 11]. Ferronickel smelting of lateritic ores is generally performed by using fossil fuels (coal, oil, natural gas, etc.) as a reductant in a rotary kiln. Nickel and cobalt are firstly reduced because iron has greater affinity to oxygen. The product is charged to converter for refining after discarding the slag phase containing unreduced iron oxide, magnesium oxide and silica. The end-product is ferronickel alloy which contains 25% of nickel. Unrefined ferronickel is refined using soda ash, calcium containing compounds to remove sulphur content. Air is blown through molten and desulphurized ferronickel to oxidize carbon, phosphorus and other impurity elements. This process is energy intensive but new furnace technologies reduce the energy costs [7, 10, 12].

Nickel pig iron (NPI) production is a new promising process, although it was firstly developed about 50 years ago but it has not been commercially used until some Chinese pig iron producers changed their production methods into NPI production. Chinese NPI production was firstly started in blast furnaces using low grade laterite ores imported from Indonesia, Philippines and New Guinea. The process is almost same as pig iron production processes. The only difference is that the ore contains more nickel. The blast furnace products contain 2-10% of nickel. A new approach is usage of electric arc furnaces to reduce operational costs [1, 2, 4, 7, 12, 13].

In this study, experiments were conducted in an induction furnace with graphite crucibles. East Anatolian Region lateritic nickel ores were employed as raw material to produce NPI. The effect of reductant ratio, process time and flux material addition was investigated.

EXPERIMENTAL STUDIES

Raw lateritic nickel ore samples which were collected from East Anatolian Region were crushed and ground by using respectively a jaw crusher, cone crusher, roller crusher and a vibratory cup mill. Average particle size of the ground ore was calculated as 303 μm by using screen analysis technique. Ore was homogenized at the end of the crushing and grinding processes.

XRD, XRF and AAS techniques were used for the characterization of the homogenized ore. Also amount of fixed carbon, volatile materials and ash in metallurgical coke were analyzed. According to X-ray diffraction results (XRD, PANalytical PW3040/60), raw ore contains mainly quartz, magnetite, hematite and magnesium chromium oxide phases and slightly nickel iron oxide. XRD pattern of the ore can be seen in figure 1.

Quantitative analysis of raw lateritic ore was performed by using AAS (Perkin Elmer Analyst 800) and XRF (Thermo SCIENTIFIC, NITON XL3t). Results are given in table 1.

The effect of the reductant amount was investigated in the first experimental set. Lateritic ore and coke were dried in a dryer at 105 °C for 120 minutes. 100 g ore and metallurgical grade coke (from 5% to 35% of charged ore) were mixed and charged into an induction furnace which is commercially designed for F9 and F10 type graphite based crucibles. Mixtures were held for 25 minutes in the induction furnace at a temperature range of 1600-1650 °C. It was observed that charged mixtures began to melt around 10^{th} minute (1350-1400 °C) and reached the maximum temperature about 15^{th}minute. Metallic and slag phases were obtained after smelting and casting step. Slags were mechanically discarded and ground. Magnetic-metallic and non-magnetic parts of the slags were separated by using magnetic separation process. Magnetic parts were added to the metallic phase for re-smelting. General flowchart of the process is given in figure 2. The homogenized metal buttons which were obtained from re-smelting stage were characterized by using XRF and AAS techniques. The most efficient experiment in recovery of Ni and Co was the mixture with 30% reductant and 100 g ore. Effect of process duration was carried out in the second experimental set. The mixture, containing 30% reductant and 100 g ore, was smelted in different process durations varying from 15 minutes to 35 minutes. The same experimental and characterization procedures and techniques as in the first experimental set were used for the second experimental set. Different amounts of CaO were added to the charge mixtures containing 10% of metallurgical coke with the process duration of 25 minutes to investigate the effect of the additive materials.

Table 1: Quantitative analysis of raw lateritic nickel ore

Ni%	**Fe,%**	**Cr,%**	**Co,%**	**Mn,%**	**Mg,%**	**Al,%**
0.90	30.11	2.30	0.054	0.31	4.99	1.80
Sr%	**Ca%**	**Zn%**	**S%**	**Ti%**	**SiO_2%**	**LOI%**
0.003	0.10	0.04	0.04	0.02	40.61	2.50

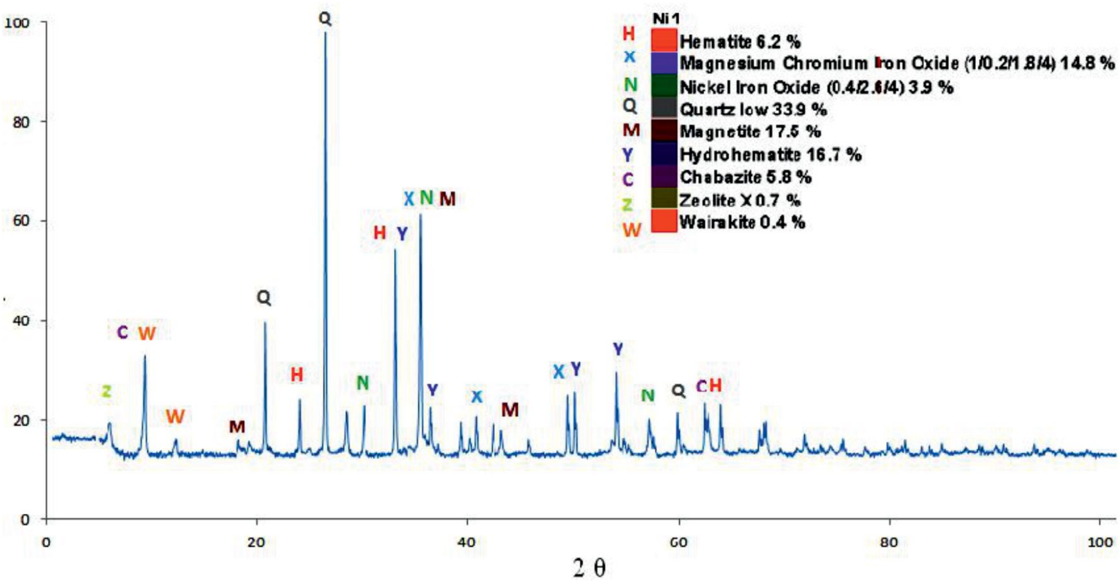

Figure 1: XRD pattern of raw lateritic nickel ore

RESULTS AND DISCUSSION

The most efficient result was taken from the experiment with 100 g ore and 30% coke mixture as 88.13% efficiency for nickel recovery in the first experimental set. The experiment with 100 g ore and 5% coke mixture had the highest nickel concentration in the metal buttons as 6.94% Ni concentration. However, nickel recovery increases with the increase in the amount of reductant, whereas nickel concentration in the alloy decreases. Ni, Co and Cr contents of the alloys are shown in table 2 and metal recovery efficiency is shown in figure 3 with increasing reductant/charged ore percentage. Oxygen affinity of Ni and Co is less than other metals in the ore so that their reduction capacities are more than others at low reductant/charged ore ratios. With increasing reductant/charged ore ratios their concentrations decrease because there is enough reductant for the reduction of other metals as can be seen in table 2 and figure 3.

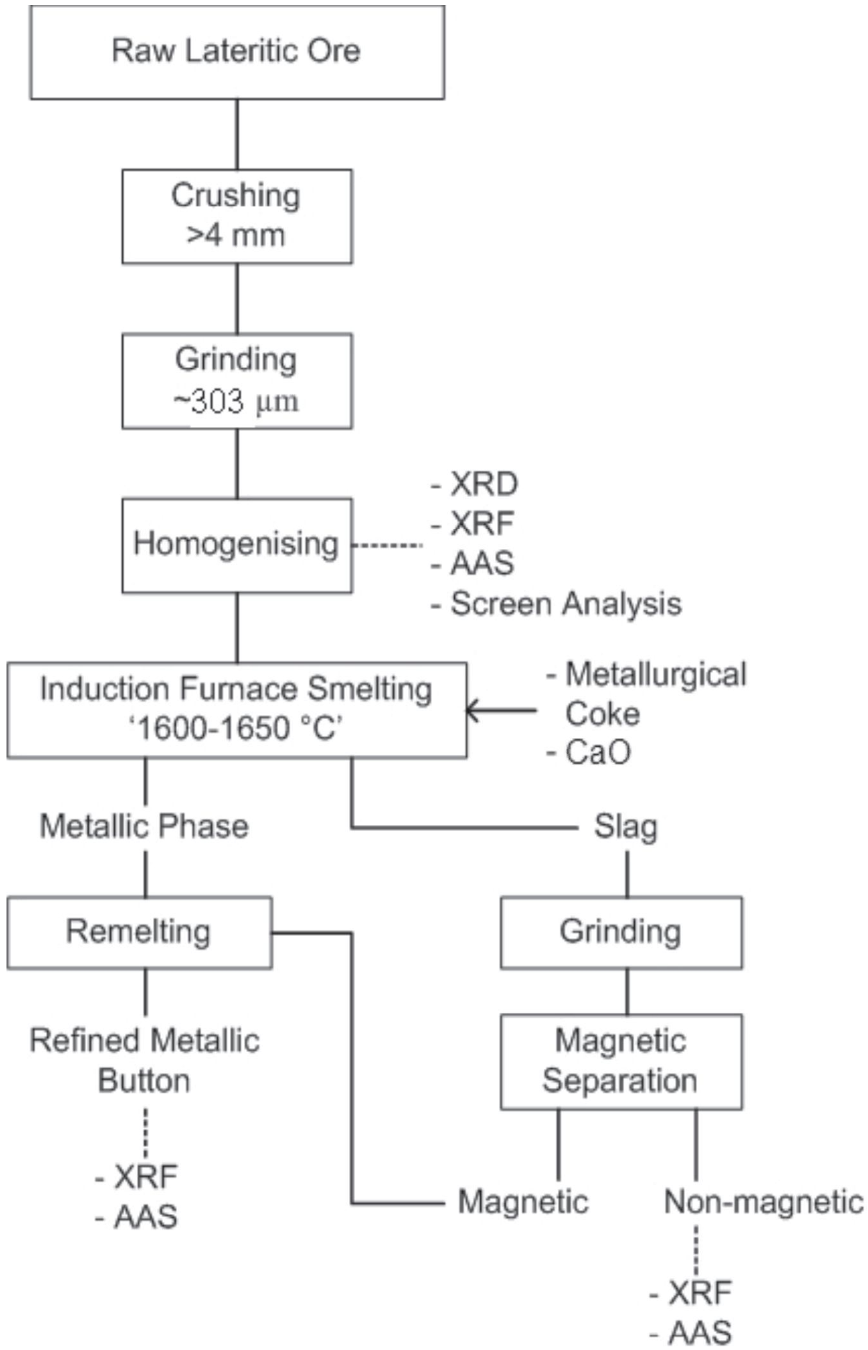

Figure 2: General flowchart of the experimental set up

Table 2: Ni, Co and Cr content of metallic buttons with different percentage of metallurgical coke/ charged ore addition for 25 minutes

Reductant / Charged Ore, %	Ni,%	Co,%	Cr,%	Fe,%
5	6.94	0.43	0.81	89.74
10	4.07	0.23	2.01	90.39
20	3.17	0.17	2.90	91.76
30	3.00	0.17	4.05	89.06
35	2.87	0.15	4.32	86.18

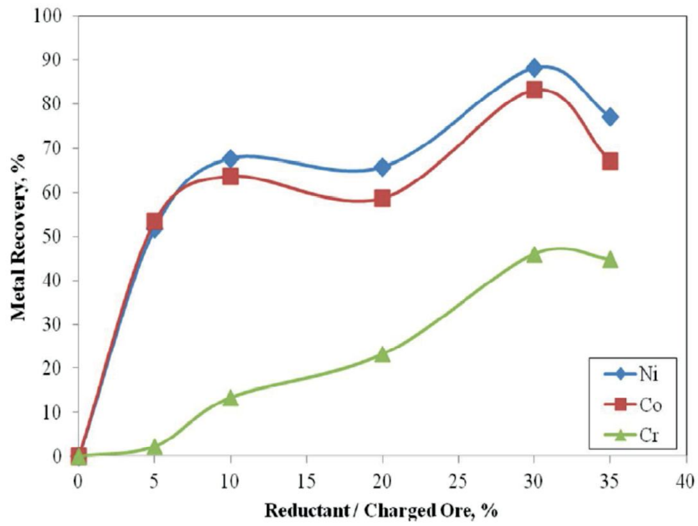

Figure 3: Ni, Co and Cr recovery efficiencies with different percentage of metallurgical coke/charged ore addition for 25 minutes

Process duration is also another important parameter that affects the metal recoveries. Efficiency in metal recovery increases with the increase of process duration as seen in table 3 and figure 4. At constant reductant/charged ore ratio (30%) Ni and Co concentration slightly changes with the increase of process duration. Ni and Co recovery increase rapidly till 25^{th} minute and Cr recovery increase till 30^{th} minute. After 30 min, metal recoveries are similar to each other.

It is observed that CaO addition increased the total metal recovery and reduced the operation temperature between 50-100 ºC to the operation temperature of 1550-1600 ºC. Experiments were conducted at 10% constant reductant/charged ore and increasing flux/charged ore ratios for 25 minutes. Ni, Co, and Cr concentrations in the obtained alloys were shown in table 4 and metal recoveries were shown in figure 5.

Table 3: Ni, Co and Cr content of metallic buttons with increasing process duration and 30% constant metallurgical coke/charged ore addition.

Duration, Min.	Ni,%	Co,%	Cr,%	Fe,%
15	3.40	0.13	4.81	91.07
20	3.09	0.22	4.99	91.19
25	3.00	0.17	4.05	89.06
30	3.25	0.24	5.54	90.80
35	3.13	0.19	5.07	91.40

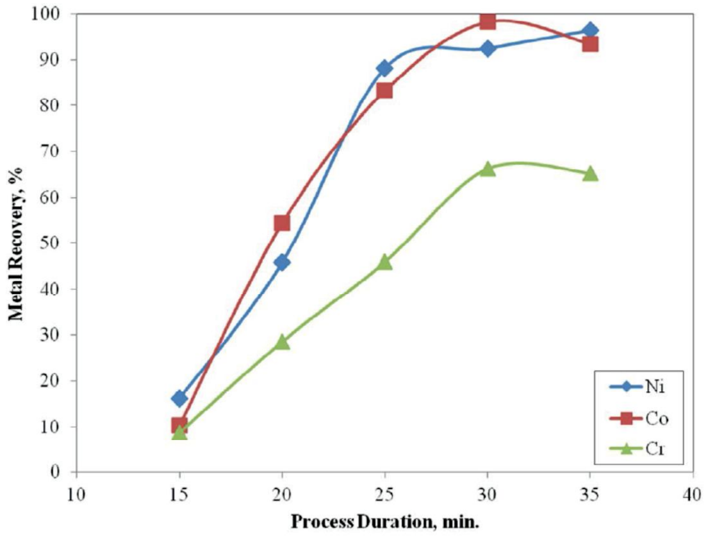

Figure 4: Ni, Co and Cr recovery efficiencies with increasing process duration and 30% constant metallurgical coke/charged ore addition

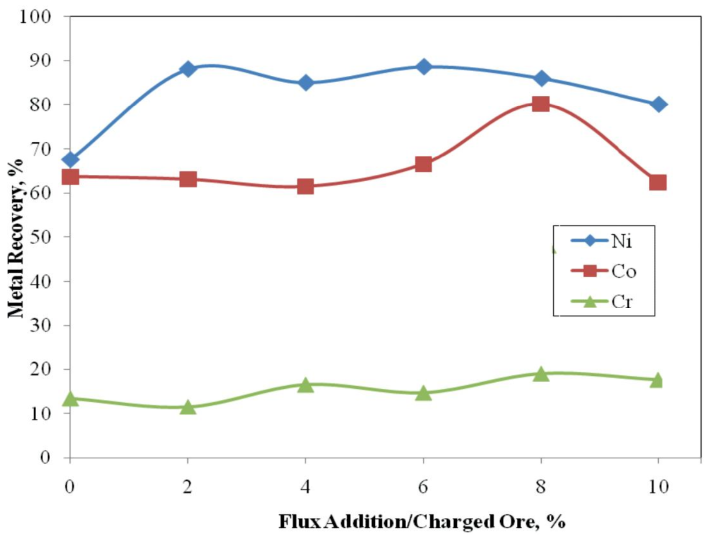

Figure 5: Ni, Co and Cr recovery efficiencies with increasing flux/charged ore ratio and 10% constant metallurgical coke/charged ore addition for 25 minutes

Table 4: Ni, Co and Cr content of metallic buttons with increasing flux/charged ore ratio and 10% constant metallurgical coke/charged ore addition for 25 minutes

Flux Addition / Charged Ore, %	Ni,%	Co,%	Cr,%	Fe,%
0	4.07	0.23	2.01	90.39
2	5.29	0.23	1.79	91.82
4	4.86	0.21	2.45	91.64
6	4.47	0.20	1.98	92.37
8	3.51	0.19	2.01	93.09
10	3.79	0.17	2.17	92.67

CONCLUSION

Nickel pig iron samples were obtained with carbothermic reduction process from East Anatolian Region lateritic nickel ores by using an induction furnace with graphite based crucibles. The effects of reductant amount, process duration and flux material amount were examined on metal recovery efficiencies and concentrations.

The highest Ni-Co recovery efficiencies were determined as 88.13% and 83.23% respectively with 30% metallurgical coke/charged ore addition for 25 minutes in the first experimental set. Same metallic button had also a satisfactory level of Cr concentration as 4.05%. The metallic button which was produced from the mixture with 5% coke had the highest Ni and Co concentration as 6.94% and 0.43% and only 0.81% Cr concentration.

Ni and Co concentrations in the alloy slightly changed with the increase of process duration but their recovery efficiencies changed rapidly with the increase in time in the second experimental set. The highest recoveries were achieved for the experiments conducted with the addition of 30% of metallurgical coke as 93.20% Ni, 93.87% Co and 65.24% Cr at the processes time of 35 minutes.

Last experimental set was designed to enhance the results obtained from the experiments with low reductant addition for the short process durations. The effect of CaO addition as a flux material was carried out. CaO addition had a beneficial effect on the metal recovery with the decrease in slag temperature. The highest recovery was achieved with 6% flux addition/charged ore as 88.58% Ni, 66.58% Co and 14.75% Cr with 10% constant reductant/charged ore addition for 25 minutes process duration.

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