ABSTRACT

Nickel finds a wide industrial application. It is obtained through extraction from nickel-containing ores. The metal extraction using a lateritic nickel ore becomes an important alternative because of nickel sulphide ore reserves decrease. This study aims to determine the coal to dolomite mass ratio that can produce ferronickel products of high nickel recovery, content, and selectivity. The extraction process studied refers to a direct reduction using a coal/dolomite bed and Na$_2$SO$_4$ as a selective agent. It takes place in a SiC crucible within 6 h at a temperature of 1300°C. The best coal to dolomite mass ratio refers to 1:2.09. It provides the highest Ni content of 12.04 %, the highest selectivity factor of 8.191 and nickel recovery of 99.1 %.

Keywords: lateritic nickel ore, coal-dolomite bed, direct reduction, selectivity factor.

INTRODUCTION

Nickel is an important alloying metal with a wide range of applications in the industry [1]. The nickel alloys have high strength and tenacity. They are characterized by high corrosion thermal resistance. The nickel laterite type ore presents about 70 % of the nickel reserve. However, only 40 % of it is processed for further application [2]. This is due to the difficulty of nickel laterite ore processing when compared to that containing nickel sulphide. It is attributed to metallic nickel uniform distribution which in turn excludes the possibility of applying flotation and gravity separation [3].

Limonitic and saprolitic types of the nickel laterite ore are present. The first one is a low nickel grade of Ni content ranging from 1.1 wt. % to 1.8 wt. % [4]. It can be processed following a hydrometallurgy route such as that of high-pressure acid leaching (HPAL) [5 - 7]. Several hydrometallurgy processes have been applied aiming limonitic nickel ore extraction but the productivity level achieved is low, while the operational costs are too high [6 - 9]. However, the nickel recovery is about 80 % and which is why the process is not economically viable [7].

Hence, many researchers have examined new methods for treating laterite nickel ore including a pyro process at a lower operating temperature, i.e. a direct reduction [10-14]. But the latter product has a low content of Ni because of the high Fe presence in the ore. Furthermore, the bond between oxygen and iron is only slightly stronger than that between oxygen and nickel, which means that FeO is reduced almost as readily as NiO [15]. So, the challenges are how to reduce selectively the Ni content of the nickel limonite ore leaving the ferrous oxide unchanged. Until now, many researchers have used several Ni selective reduction procedures. Some of them have applied Na$_2$SO$_4$ as an additive [16, 17]. The investigation reported is focused on using a bed of a mixture of coal and dolomite and Na$_2$SO$_4$ as a selective agent varying the coal to dolomite mass ratio because of its effect on CO to CO$_2$ mole ratios obtained in the course of the coal and the dolomite heating.
EXPERIMENTAL

Materials

Raw materials of limonite nickel ore of a 50 mesh standard size were obtained from Southeast Sulawesi, Indonesia. The coal used was obtained from south Borneo, Indonesia, while the dolomite was a product of Gresik, East Java, Indonesia. The chemical composition of the nickel ore was characterized by EDX and the results obtained are shown in Table 1. The proximate data referring to the contents of the coal used in this research is shown in Table 2. The chemical composition of dolomite was characterized by EDX. The results obtained are listed in Table 3.

Na\textsubscript{2}SO\textsubscript{4}, starch, and demineralized water used in this investigation were of a chemical grade.

Methods

All raw materials (the limonite nickel ore, the coal, and the dolomite) were crushed and sieved aiming 50 mesh standard sieve. Na\textsubscript{2}SO\textsubscript{4} powder was introduced to the mixture containing the ore and the coal. Then, the starch and demineralized water (50 ml) were added to the mixture. The latter was pressed to form pillow briquettes using a pressure of 30 kg/cm\textsuperscript{2}. They were then dried for 3 h at 110\textdegree C. The mass of all raw materials is shown in Table 4. The mass of the bed components is shown in Table 5. The values of the CO/CO\textsubscript{2} mole ratio are chosen on the ground of refs. [18, 19].

The briquettes were inserted in the bed placed in a muffle furnace crucible. The bed covered all the briquettes. Then, the temperature of the furnace was...
increased to 1400°C and was held at this value for 6 h. After the furnace was cooled, the briquettes were taken out, crushed and subjected to a magnetic separation. Then, they were characterized by EDX and XRD. Fig. 1 illustrates the direct reduction process used.

RESULTS AND DISCUSSION

Fig. 2 (a) shows the effect of the coal-dolomite mass ratio on the recovery of Ni and Fe. The increase of the coal/dolomite mass ratio brings about an increase of the nickel recovery. In fact, the nickel recovery increases in the case of all ratios used. This is attributed to nickel oxide reduction to nickel. It is worth adding that sulphur also increases the nickel recovery [20].

Fig. 2(b) shows that the increase of the coal/dolomite mass ratio results also in an increase in iron recovery. Hence, this factor affects both metals recovery as the latter is determined by the amount of the reductant. This, in turn, indicates that the possibility of Boudouard reaction proceeding is high because of CO and CO$_2$ accommodation. The Boudouard reaction is described [21] by Eq. 1:

$$\text{CO}_2 \text{ (from reduction product and dolomite decomposition)(g)} + \text{C (from coal)(s)} \rightarrow 2\text{CO (g)}$$

(Eq.1)

![Fig. 1. A schematic presentation of the direct reduction installation (all dimensions in mm).](image1)

![Fig. 2. An effect of the coal/dolomite mass ratio on (a) Ni recovery and (b) Fe recovery in the product obtained.](image2)
Based on this reaction, CO reduces nickel and iron oxides to nickel and iron. Besides, it is known that the decrease of the coal/dolomite mass ratio leads to an increase of olivine \((\text{Mg,Ni})_2\text{SiO}_4\) formation, which in turn indicates that Ni will be included in the non-magnetic portion and its recovery will be decreased. It can be seen that the recovery of Fe is lower than that of Ni in all cases, which leads to the assumption that the corresponding reduction reaction is inhibited.

Fig. 3(a) shows that the initial Ni content in the limonite nickel ore is 1.25%. After the reduction process at 1400°C, the product’s Ni content increases at all values of the coal/dolomite mass ratio. This is caused by the decomposition reaction of goethite \((\text{Fe,Ni})\text{OOH}\) present in the ore. It is connected with dehydroxylation of the goethite OH- structure. The reaction [19] considered is presented by Eq. 2:

\[
2(\text{Fe,Ni})\text{O.OH} \rightarrow (\text{Fe,Ni})_2\text{O}_3 + \text{H}_2\text{O} 
\]  

(2)

The dehydroxylation increases also the specific surface area as the goethite structure opens up and the nickel present can be set free [22]. Then, CO obtained by the Bouduard reaction reduces \(\text{Fe}_x\text{O}_y\) and \(\text{NiO}\) providing Fe and Ni. In fact, the increase of Ni content in the product is determined by its selective reduction. The latter is affected by the reaction of Fe with S contained in \(\text{Na}_2\text{SO}_4\). The reactions [17] taking place are presented by Eqs. 3 - 7:

\[
\text{Na}_2\text{SO}_4 + 4\text{CO} \rightarrow \text{Na}_2\text{S} + 4\text{CO}_2 
\]  

(3)

\[
\text{Na}_2\text{SO}_4 + 3\text{CO} \rightarrow \text{Na}_2\text{O} + \text{S} + 3\text{CO}_2 
\]  

(4)

\[
\text{Na}_2\text{O} + 2\text{Fe}_2\text{SiO}_4 \rightarrow 4\text{FeO} + \text{Na}_2\text{Si}_2\text{O}_5 
\]  

(5)

\[
\text{Fe} + \text{S} \rightarrow \text{FeS} 
\]  

(6)

\[
\text{Na}_2\text{S} + \text{FeO} + 2\text{SiO}_2 \rightarrow \text{FeS} + \text{Na}_2\text{Si}_2\text{O}_5 
\]  

(7)

Fig. 3(a) shows also that a high Ni content of the product is obtained in case of a coal/dolomite mass ratio of 1.48:1 (Sample B). In this case, the CO/\(\text{CO}_2\) mol ratio is the highest. Its value equals 2.23 as evident from Table 5. This means that sample B has a higher CO/\(\text{CO}_2\) mol ratio than that of samples A and D. On the other hand, the Ni content of sample B is slightly higher than that of sample C, which is caused by the formation of jadeite \(((\text{Al, Ca, Fe, Na})\text{Si}_2\text{O}_6)\). The \(\text{Fe}^{3+}\) ion is entrapped in the jadeite structure. Fig. 2(b) shows that the Fe recovery of sample B is lower than that of sample C. The wt. % of Fe of sample C is lower than that of sample B as shown in Fig. 3(b). This is attributed to the CO/\(\text{CO}_2\) mol ratio of sample B which is higher than that of sample C. It facilitates the reaction (Eq.3) proceeding in sample B. On the other hand, the reaction described by Eq. 4. takes place faster in sample C. As a result, S diffuses into the FeNi lattice of sample C product. As a result, the latter content of S will be higher than that of sample B. Hence,
the Fe content of sample C is slightly lower than that of sample B product.

Fig. 4 shows the phases formed in the metal product obtained in the course of the direct reduction. Fig. 4 verifies that metals are obtained as products in case of all coal/dolomite mass ratios studied. The metal phases refer to Fe, FeNi, and Fe$_5$Si$_3$ when the coal/dolomite mass ratio is equal to 1.19:1, as shown in Fig. 4(a). The metal phases refer to Fe and FeNi in case of a coal/dolomite mass ratio of 1.48:1. This is illustrated in Fig. 4(b). When the ratio investigated has a value of 2.09:1, the metal phases refer to Fe, Ni, and Fe$_5$Si$_3$.

So, it can be concluded that Ni and Fe oxide reduction proceeds at all ratios studied. It can also be concluded that in case of a coal/dolomite mass ratio of 2.09:1, the elements of FeNi alloy are separated, i.e. the alloy is not existing any longer. This is consistent with the results presented in Fig. 2(a) - the highest coal/dolomite mass ratio brings about the highest recovery of Ni. The reason is that Ni and Fe have been separated. Besides, the reduction atmosphere of the crucible affects also the separation of the metals produced. There is an optimal reduction atmosphere (CO/CO$_2$ ratio), which is required. The CO/CO$_2$ mol ratio, in this case, is equal to 1.56:1. FeNi alloy is the product of the reduction proceeding at lower ratio values. But the same is valid in case of higher mol ratios of CO/CO$_2$. Hence, it follows that the latter factor affects not only the selective reduction but also the separation of the metals considered. To compare the results obtained with those of studying the selective reduction of the laterite nickel ore by a carbothermic reduction process, the so-called selectivity equation is used. It is connected with the evaluation of the selectivity factor by Eq. 8:

$$\beta_{Ni} = \frac{X_{Ni}}{X_{Fe}} \frac{Y_{Fe}}{Y_{Ni}}$$  \hspace{1cm} (8)

where X and Y are the grades of Ni and Fe in the unreduced and the reduced ore, respectively. The selective reduction of Ni using ores of varying Ni and Fe grades can be compared [23] on the ground of the Eq. 8 application.

The selectivity factor obtained at all values of the ratios studied is shown in Fig. 5.

The best selectivity reduction of Ni is obtained when using a coal/dolomite mass ratio of 1.48:1. The value found is slightly higher than that in the case of using a 2.23:1 ratio. But, it is much higher than the value estimated in the experiment with a ratio of 1.19:1. So, it can be concluded that the coal/dolomite mass ratio of 1.48:1 is the best for Ni selective reduction. A comparison of the selectivity factor values obtained in other investigations is shown in Table 6.

It is worth adding that the Al$_8$Fe$_2$Si phase is formed on the product surface in the course of all experiments carried out, i.e. at all coal/dolomite mass ratio values used.
CONCLUSIONS

A direct reduction of limonitic laterite nickel ore using a mixed dolomite-coal bed and Na$_2$SO$_4$ as a selective reduction agent is successfully carried out. The best ferronickel metal can be obtained using a coal/dolomite mass ratio of 1:2.09. In this case, a high recovery and a high selectivity factor in respect to Ni are obtained. The ferronickel product contains 12.04% of Ni, while its recovery amounts to 99.1%. The best selectivity factor of this method amounts to 8.191.

REFERENCES