

## Direct Reduction Of Nickel Laterite Limonitic Ore Using A Coal-Dolomite Mixture Bed And $\text{Na}_2\text{SO}_4$ as A Selective Agent

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### 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  $\text{Na}_2\text{SO}_4$  as a selective agent. It takes place in a SiC crucible within 6h at a temperature of  $1300^\circ\text{C}$ . 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.

### I. 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 reprocessing 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  $\text{Na}_2\text{SO}_4$  as an additive [16, 17]. The investigation reported is focused on using a bed of a mixture of coal and dolomite and  $\text{Na}_2\text{SO}_4$  as a selective agent varying the coal to dolomite mass ratio because of its effect on CO to  $\text{CO}_2$  molar ratios obtained in the course of the coal and the dolomite heating.

## II. 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<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>SO<sub>4</sub> 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<sup>2</sup>. They were then dried for 3 h at 110°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<sub>2</sub> molar 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

Table 1. Results of limonite nickel ore chemical composition.

Elements	Ni	Fe	Si	Mg	Ca	Al	Cr	Mn	Co
wt. %	1.25	55.37	1.94	0.42	0.46	5.04	1.54	0.88	1.62

Table 2. Proximate results referring to the contents of the coal used.

Parameters	Results	Unit	Testing standards
Total moisture	1.8	%, ar <sup>*</sup> )	ASTM D3302-02
Ash content	4.75	%, ar	ASTM D3174-02
Fixed carbon	42.35	%, adb <sup>*</sup> )	ASTM D3175-02
Volatile matter	52.86	%, adb	ASTM D3172-02

\* ar - a received sample; adb - a dry basis sample.

Table 3. Results of dolomite chemical composition.

Elements	Ca	Mg	C	O
wt. %	18.01	14.30	12.62	55.07

Table 4. Raw materials used for briquettes production.

A sample code	A coal/dolomite mass ratio	An estimated CO/CO <sub>2</sub> mole ratio	Limonite nickel ore (g)	Coal (g)	Na <sub>2</sub> SO <sub>4</sub> (g)	Starch (g)	A briquette total mass (g)
A	1.19:1	0.88	100	27.07	14.42	4.24	168.57

B	1.48:1	2.23	100	68.36	14.42	4.24	233.22
C	2.09:1	1.56	100	47.71	14.42	4.24	189.21

Table 5. Bed raw materials used.

A sample code	A coal/dolomite	An estimated CO/CO <sub>2</sub> mole ratio	Coal (gr)	Dolomite (g)	A briquette total mass (g)
A	1.19:1	0.88	27.07	22.84	168.57
B	1.48:1	2.23	68.36	46.20	233.22
C	2.09:1	1.56	47.71	22.84	189.21

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.

### III. 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

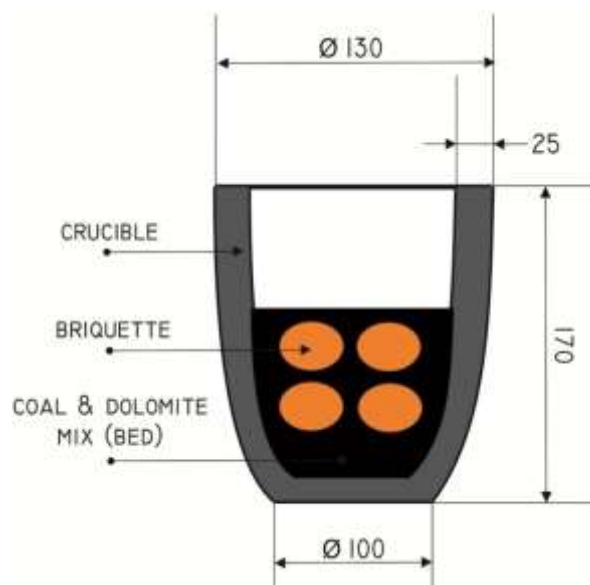
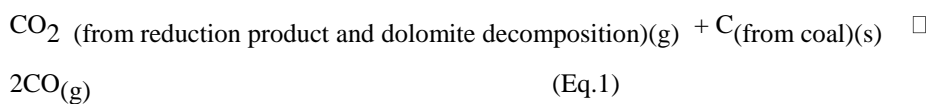
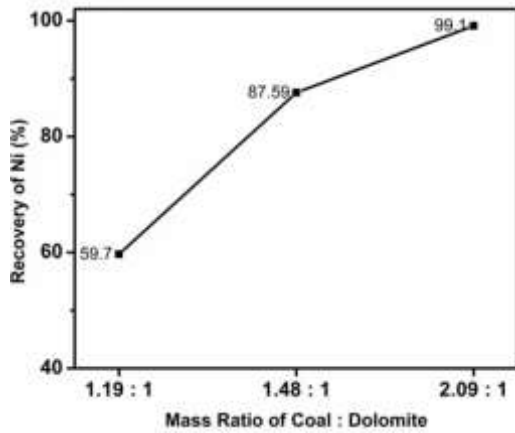


Fig. 1. A schematic presentation of the direct reduction installation (all dimensions in mm).

turn, indicates that the possibility of Boudouard reaction proceeding is high because of CO and CO<sub>2</sub> accommodation. The Boudouard reaction is described [21] by Eq. 1:

proceeding is high because of CO and CO<sub>2</sub> accommodation.





(b)

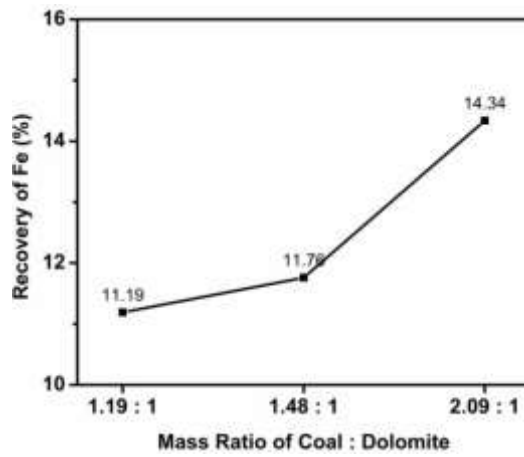
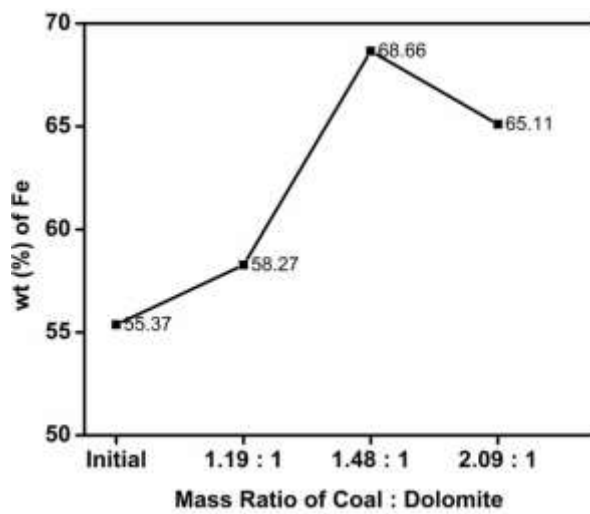
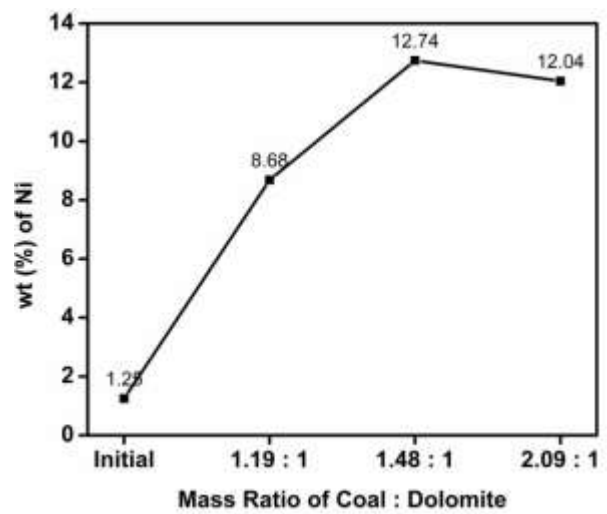


Fig. 2. An effect of the coal/dolomite mass ratio on (a) Ni recovery and (b) Fe recovery in the product obtained.



(a)

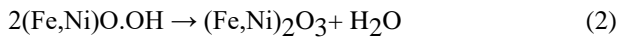


(b)

Fig. 3. An effect of the coal/dolomite mass ratio on the product content (in wt. %) of (a) Ni and (b) Fe.

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 ((Mg,Ni)<sub>2</sub>SiO<sub>4</sub>) 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 ((Fe,Ni)OOH) present in the ore. It is connected with dehydroxylation of the goethite OH-structure. The reaction [19] considered is presented by Eq. 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 Boudouard reaction reduces Fe<sub>2</sub>O<sub>3</sub> and 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 Na<sub>2</sub>SO<sub>4</sub>. The reactions [17] taking place are represented by Eqs. 3 - 7:

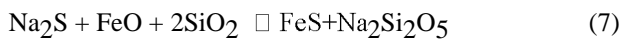
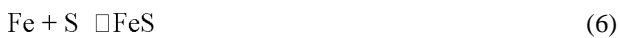
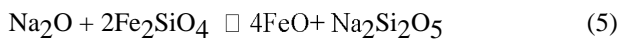
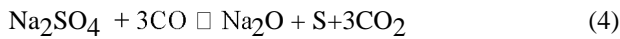


Fig. 3(a) shows also that a high Ni content of the product is obtained in case of a coal/dolomite mass ratio of 1.48:1 (Sample B). In this case, the CO/CO<sub>2</sub> mol ratio is the highest. Its value equals 2.23 as evident from Table 5. This means that sample B has a higher CO/CO<sub>2</sub> mol ratio 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 ((Al, Ca, Fe, Na)SiO<sub>3</sub>). The Fe<sup>3+</sup> 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/CO<sub>2</sub> 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,

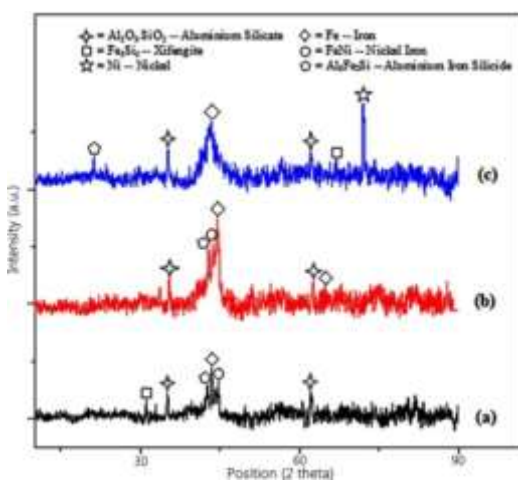


Fig. 4. An effect of the coal/dolomite mass ratio on the phase of the metal product: (a) a ratio of 1.19:1, (b) a ratio of 1.48:1 and (c) a ratio of 2.09:1.

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<sub>5</sub>Si<sub>3</sub> 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<sub>5</sub>Si<sub>3</sub>.

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<sub>2</sub> ratio), which is required. The CO/CO<sub>2</sub> mol ratio, in this case, is equal to 1.56:1. FeNi alloy is the product of the reduction proceeding at low ratio values. But the same is valid in case of higher mol ratios of CO/CO<sub>2</sub>. 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:

$$\beta_{\frac{Ni}{Fe}} = \frac{X_{Ni}}{X_{Fe}} \frac{Y_{Fe}}{Y_{Ni}} \quad (8)$$

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<sub>8</sub>Fe<sub>2</sub>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.

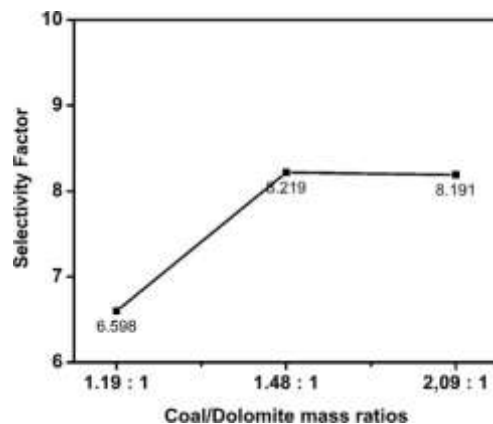


Fig. 5. A selectivity factor obtained at all values of the ratios studied.

Table 6. A comparison of the selectivity factor values obtained in the course of other investigations.

No	Nickel ore type	Methods	Selectivity Factors	References	Year
1	Saprolite	Reduction roasting using coal as a reducing agent and Na <sub>2</sub> SO <sub>4</sub> as an additive	21.8	Jiang, M.[17]	2013
2	Saprolite	Semi-molten state reduction using anthracite coal as a reducing agent and CaO as flux	1.34	Liu, M. [13]	2014
3	Saprolite	Direct reduction using anthracite coal as a reducing agent and NaCl as an additive	1.25	Zhou, S. [19]	2016
4	Limonite	Direct reduction using bio coal mixed in pellet, no additive used	1.06	Chen, G.J. [21]	2014
5	Limonite	Direct reduction using bituminous coal, with elemental sulphur as an additive	1.69	Elliot, R.[23]	2015
6	Limonite	Direct reduction using sub-bituminous coal and Na <sub>2</sub> SO <sub>4</sub> as additive with the variation of holding time (The best holding time was 8 hours)	6.08	Abdul, F. [25]	2018
7	Limonite	Direct reduction using sub-bituminous coal and Na <sub>2</sub> SO <sub>4</sub> as an additive with the variation of temperature (The best temperature was 1400 <sup>0</sup> C)	3.07	Abdul, F. [26]	2018
8	Limonite	Direct reduction using coal-dolomite bed and Na <sub>2</sub> SO <sub>4</sub> as an additive	8.191	Present Study	2018

#### IV. CONCLUSIONS

A direct reduction of limonitic laterite nickel ore using a mixed dolomite-coal bed and Na<sub>2</sub>SO<sub>4</sub> 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 amount is 99.1%. The best selectivity factor of this method amounts to 8.191.

#### REFERENCES

- [1] R.R. Moskalyk, A.M. Alfatanzhi, Nickel laterite processing and electrowinning practice, Minerals Engineering, 15, 2002, 593-605
- [2] A.D. Dalvi, W.G. Bacon, R. Osborne, The past and the future of nickel laterites, Proceeding PDAC 2004 International Convention Trade Show & Inventors, Ontario, Canada, 2004.
- [3] T. Norgate, S. Jahanshahi, Accessing the energy and greenhouse gas footprint of nickel laterite processing, Minerals Engineering, 24, 2011, 698-707.
- [4] G.X. Qiu, Q.X. Shi, Research on reduction and enrichment of ferronickel from laterite-nickel ores using carbon as reductant, Mining and Metallurgical Engineering, 29, 2009, 75-77.
- [5] B.I. Whittington, D. Muir, Pressure acid leaching of nickel laterites: A Review, Min. Process. Extractive Metall. : Int. J. 21, 6, 2000, 527-599.
- [6] J. Kyle, Nickel laterite processing technologies – where to next? In: ALTA 2010 Nickel/Cobalt/Copper Conference, Perth, Western Australia, 2010.

- [7] C.A.Pickles, J.Forster, R.Elliot, Thermodynamic analysis of the carbothermic reduction roasting of a nickeliferous limonitic laterite ore, *Miner. Eng.*, 65, 2014, 33-40.
- [8] M.G.King, Nickel laterite technology - finally a new dawn?, *JOM*, 57, 7, 2005, 35-39.  
A. Oxley, N.Barca, Hydro-pyrometallurgical processing of nickel laterites, *Miner. Eng.* 54, 2013, 2-13.
- [9] J. Kim, G. Dodbiba, H. Tanno, K. Okaya, S.Matsuo,
- [10] T.Fujita, Calcination of low-grade laterite for concentration of Ni by magnetic separation, *Miner. Eng.*, 23, 2010, 282-288.
- [11] Y. Li, Y. Sun, Y. Han, P. Gao, Coal-based reduction mechanism of low-grade laterite ore, *Trans. Nonferrous Met. Soc. China*, 23, 2013, 3428-3433.
- [12] G. Zheng, D. Zhu, J. Pan, Q. Li, Y. An, J. Zhu, Z. Liu, Pilot scale test of producing nickel concentrate from low-grade saprolitic laterite by direct reduction-magnetic separation, *J. Cent. South Univ.*, 21, 2014, 1771-1777.
- [13] M.Liu, X.LV, E.Guo, P.Chen, Q.Yuan, Novel process of ferronickel nugget production from nickel laterite by semi-molten state reduction, *ISIJ International*, 54, 8, 2014, 1749-1754.
- [14] S. Chen, S.Q. Guo, L. Jiang, Y.L. Xu, W.Z. Ding, Thermodynamic of selective reduction of laterite ore by reducing gases, *Trans. Nonferrous Met. Soc. China*, 25, 2015, 3133-3138.
- [15] F. Crundwell, W.G. Davenport, V. Ramachandran, M. Moats, T. Robinson, *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*, Elsevier, Oxford, UK, 2011, p.51.
- [16] G.H. Li, T.M. Shi, M.J. Rao, T. Kiang, Y.B. Zhang, Beneficiation of nickeliferous laterite by reduction roasting in the presence of sodium sulfate, *Miner. Eng.* 32, 2012, 19-26
- [17] M. Jiang, T. Sun, Z. Liu, J. Kou, N. Liu, S. Zhang, Mechanism of sodium sulfate in promoting selective reduction of nickel laterite ore during reduction roasting process, *International Journal of Mineral Processing*, 123, 2013, 32-38.
- [18] C.J. Hallet, A Thermodynamic analysis of the solid state reduction of nickel from laterite minerals, *Proceeding of nickel-cobalt 97 International Symposium Pyrometallurgical Fundamentals and Process Development*, Sudbury, 1997, 299-312.
- [19] R.Elliot, C.A.Pickles, J.Forster, Thermodynamic of The Reduction Roasting of Nickeliferous Laterite Ore, *Journal of Minerals and Materials Characterization and Engineering*, 4, 2016, 320-346.
- [20] F.Rodrigues, C.A.Pickles, J.Peacey, R.Elliot, J.Forster, Factors affecting the upgrading of nickeliferous limonitic laterite ores by reduction roasting, thermal growth and magnetic separation, *Minerals*, 176, 7, 2017, 1-21.
- [21] G.J. Chen, W.S. Hwang, S.H. Liu, J.S. Shiau, I.G. Chen, Effect of reduction temperature on the carbothermic reduction process of laterite ores mixing with bio-coal, *METAL*, Brno, Czech Rep., 2014.
- [22] F. O'Connor, W.H. Cheung, M. Valix, Reduction roasting of limonite ores : effect of dehydroxylation, *International Journal of Mineral Processing*, 80, 2006, 88-99.
- [23] R.Elliot, F.Rodrigues, C.A.Pickles, J.Peacey, A two-stage thermal upgrading process for nickeliferous limonitic laterite ores, *The Canadian Journal of Metallurgy and Materials Science*, 54, 2015, 1-11.
- [24] S. Zhou, Y. Wei, B. Li, H. Wang, B. Ma, C. Wang, Mechanism of sodium chloride in promoting reduction of high-magnesium low nickel oxide ore, *Scientific reports* 6 : 29061, 2016, 1-12.
- [25] F.Abdul, S.Pintowantoro, R.B. Yuwandono, Analysis of holding time variations to Ni and Fe content and morphology in nickel laterite limonitic reduction process by using coal-dolomite bed, *AIP Conference Proceedings*, 2018, 020033.
- [26] F.Abdul, S.Pintowantoro, A.Kawigraha, A.Nursidiq, Effects of reduction temperature to Ni and Fe content and the morphology of agglomerate of reduced laterite limonitic nickel ore by coal-bed method, *AIP Conference Proceedings*, 2018, 020034.